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DETECTION OF ARSENIC IN GROUNDWATER OF LAKSAR AREA, HARIDWAR DISTRICT, UTTARAKHAND

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ABSTRACT

Arsenic (As) is one of the most common elements in the earth's crust and is commonly found in many locations at varying concentrations. Various researchers reported that elevated As (more than 10 µg/L) is widely present in the potable groundwater worldwide. In India, higher concentration of As has been mainly reported in the state of West Bengal, Bihar and Uttar Pradesh (river Ganga passes through these states). The present study has been carried out in Laksar block of Haridwar district, Uttarakhand as the selected study area has not been investigated with reference to arsenic. Previous studies concluded that main source of As occurrence in Gangetic plain is due to Himalayan sediment carried out and deposited by Ganga river. Keeping in mind the above assumption, authors attempted to study the physico-chemical characteristics with special emphasis on As in groundwater of the study area which is located just below the Shivalik foothills of Himalaya. Arsenic concentration in Laksar area, Haridwar is reported for the first time based on the investigations carried out in the present study. Arsenic concentration ranges from below detectable limit (BDL) to 84.0 ppb. The enrichment was encountered in the sampling sites that are close to the flood plain of Solani (a tributary of river Ganga) and Ganga river. The arsenic concentration in ~37% samples exceed the acceptable limit (10 ppb) and 6% of groundwater samples i.e. at two locations (namely Dausni Railway Fatak and Fatwa village) exceed the permissible limit (50 ppb) of drinking water standard as prescribed by BIS, 2012. The samples which show As concentration more than 10 ppb are generally tends to have negative ORP suggesting anoxic/anaerobic conditions in the aquifer. The hydro-geochemical facies of groundwater can be broadly classified as Ca–Mg-HCO_3 type.

Keywords: *Arsenic, Haridwar, groundwater, Uttarakhand, Ganga river*

INTRODUCTION

Groundwater is the most important source of domestic, industrial and agricultural water supply in the world. It is estimated that approximately one third of the world's population uses groundwater for drinking purpose (Nickson et al. 2005). Generally, groundwater quality depends on the quality of recharged water, atmospheric precipitation, inland surface water and subsurface geochemical processes (Kumar et al. 2016). Arsenic (As) contamination of groundwater is currently one of the largest public health crises that the world faces. Elevated concentrations of arsenic in drinking water (above 50 µg/L) have been reported in several countries, including Bangladesh, India, Argentina, Chile, China, Mongolia, Taiwan, Nepal, Japan, Mexico, Poland, Vietnam, and the USA etc. Arsenic is found in the natural environment in the Earth's crust, water and air. Weathering processes of rocks and minerals appears to be a major source of arsenic found in soils and the arsenic concentration is usually higher in soils than in parent rocks. Under typical soil forming conditions, the nature of arsenic in soil is controlled by the lithology of parent rock materials, volcanic activity, bioactivity, weathering, etc. There are various studies focusing to Ganga-Brahamputra-Meghna basin including lower gangetic (Nickson et al. 2005; Singh et al. 2014) basin and few studies have been carried out in central gangetic basin (U.P and Bihar), where high concentration of As is reported (Ramanathan et al. 2006; Saha et al. 2010). There are limited studies related to arsenic in the upper Ganga basin and no study has been carried out in the state of Uttarakhand as per author's knowledge. The present study was carried out in upper Ganga plain (Laksar, Haridwar, Uttarakhand) as the selected study area has not been examined with reference to arsenic. The present study aims at investigation of physico-chemical characteristic with special emphasis on as in shallow aquifer situated along the Ganga and Solani river plains of the study area.

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STUDY AREA

Study area is Laksar block lying in the south-eastern part of the Haridwar district of Uttarakhand, (Fig.1) located at 29.749°N, 78.024°E. The study area has hot, sub-humid (dry), moderate subtropical to humid climate. The average normal annual rainfall in the study area is 1174.3 mm (avg. normal annual rainfall of study area is considered same as of Haridwar district), out of which 84% is received during monsoon season (CGWB, 2016). River Ganga and its tributaries Solani river (originates from Shiwalik series), Ratmau and Banganga form the major drainage of the study area. Most of these tributaries are seasonal only and go dry after the monsoon season. The overall drainage is controlled by the Ganga river and it flows from North to South in the study area. The recent sediments deposited by these rivers locally known as Khadar. It consists of mainly fine sand, silt and clay. Ground water occurs in this area in unconfined condition at very shallow depth. The pre-monsoon depth to water level in the study area ranges between 4.38 to 5.69 m bgl and in post-monsoon it varies from 2.32 to 2.53 m bgl respectively (CGWB, 2016).

APPROACH AND METHODOLOGY

Thirty three representative groundwater and two surface water samples have been collected by making grid of size 3 km x 3 km from the tube-well/hand pump of varying depth, Ganga and Solani rivers during pre-monsoon (April), 2019. All the samples collected from Laksar block except three samples which are falling in Kuwakheda village (boundary of Laksar and Khanpur block) of Khanpur block of Haridwar district. The information about the age of the tube wells/HPs was collected from local people and the range varies from 1 to 20 years, with an average of 8 years. Similarly, the information about the depth of the tube well/HP was collected from its users and generally depth varies from 10 m to 50 m. Samples were collected in HDPE bottles after a thorough purging of hand pump (at least 10 minutes) for major ion chemistry and trace metal analysis. The in-situ parameters (pH, electrical conductivity (EC), dissolved oxygen (DO) and oxidation-reduction potential (ORP)) were measured using Hach multi-parameter analyzer (Model No. HQ 40 d). The samples were collected in bottles after filtering through a 0.45 µm membrane filter paper. Major Cations (Ca, Mg, Na, K) and major anions (HCO_3, Cl, SO_4, NO_3) were analyzed using Ion-Chromatography (Model No. Dionex ICS-5000) and trace metals (As, Fe and Mn) were measured using ICP-OES (Model No. Agilent-VDV-5110). All the parameters were analysed following the standard procedure of APHA, 2012.

RESULTS AND DISCUSSION

pH, EC, DO and ORP

pH measures the intensity of acidity or alkalinity on a scale ranging from 0-14. The pH of water samples of the study area varies from 7.1 to 8.3 (Fig. 2) with an average value of 7.65 and are well within the limits prescribed by BIS (2012) for drinking water. pH for Ganga and Solani river was measured 8.4 and 8.2 respectively which are alkaline in nature. EC is a measure of the ability of an aqueous solution to carry an electric current. The ability of carrying current depends on the presence of ions and their total concentration, mobility and the water temperature of measurement. The EC varies from 400 to 1591 μScm^{-1} (Fig. 2) with an average value of 829 μScm^{-1} in groundwater. EC for Ganga and Solani river are 208 and 585 μScm^{-1}

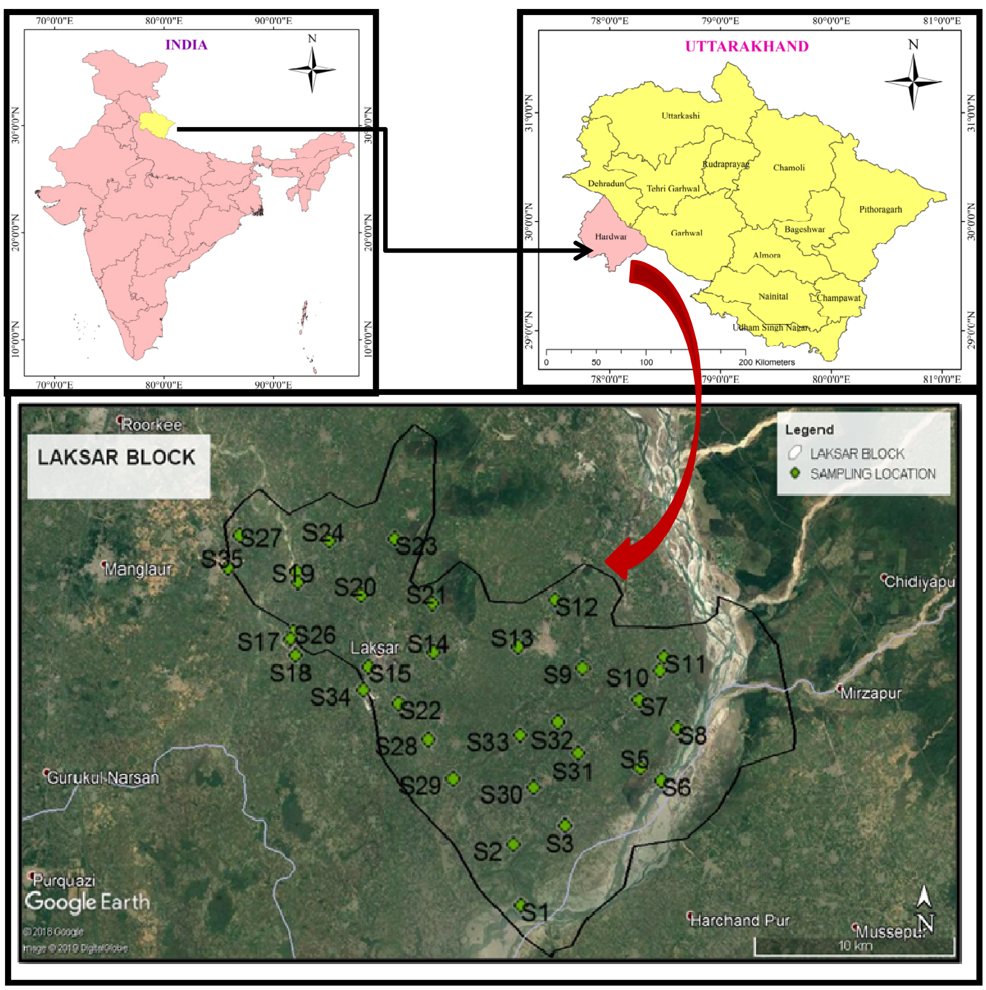

Fig.1: Geographical location map of the Laksar area with sampling locations

respectively. DO concentration has a significant effect upon ground water quality by regulating the valence state of trace metals and by constraining the bacterial metabolism of dissolved organic species. For these reasons, the measurement of dissolved oxygen concentration should be considered essential in water quality investigations. The DO values varies from 1.2 to 4.2 ppm with an average value of 2.1 ppm in groundwater. DO for Ganga and Solani rivers are 8.2 and 7.1 ppm respectively. ORP is an indicator of redox condition of groundwater. Reductive desorption is part of a chemistry reaction known as “redox”, which stands for reduction and oxidation. Various studies suggested that the release of arsenic into groundwater from soil particles occurs mainly as a result of reductive desorption. When the soil particles that have arsenic bonded to them are reduced, the arsenic is released into the groundwater. ORP was measured in-situ and it ranges from -182 to 175.0 mV with average value of -34 mV in groundwater samples while in Ganga and Solani river ORP value was found to be 36.5 and 72.3 mV respectively. The samples which shows As concentration more than 10 ppb are generally tends to have negative ORP suggesting anoxic/anaerobic conditions in the aquifer.

Major Cations and Anions

The chemical characteristic of groundwater is presented in Table 1. The water chemistry of the area is dominated by alkaline metals. On an average, Ca^{++} alone constitutes 40.9 % of the total cations (TZ^{+}) in the groundwater of the study area. Calcium is dominant cation followed by Mg (21.6%), K (19.5 %) and Na (18%). The anion chemistry of the analyzed samples shows that HCO_3^- is the dominant anion and follow the abundance order of HCO_3^- (75.1%)> Cl^- (11.3%) > SO_4^{2-} (10.7%) >NO_3^-(2.4%)>F^- (0.1) in majority of the groundwater samples. In the study area, concentration of calcium in groundwater varies from 24 mg/l to 128 mg/l with an average concentration value of 54 mg/l, whereas Ca concentration in Ganga and Solani rivers are 22 mg/l and 44 mg/l respectively. About 91% of samples are within the acceptable limit while 9 % samples exceed the acceptable limit but within permissible limit for drinking water prescribed by BIS (2012). High concentration of Ca^{2+} in the study area might have come from dissolution of calcite i.e., due to carbonate weathering. The concentration of Mg in groundwater varies from 10 mg/l to 49 mg/l with an average concentration value of 29 mg/l, whereas Mg concentration

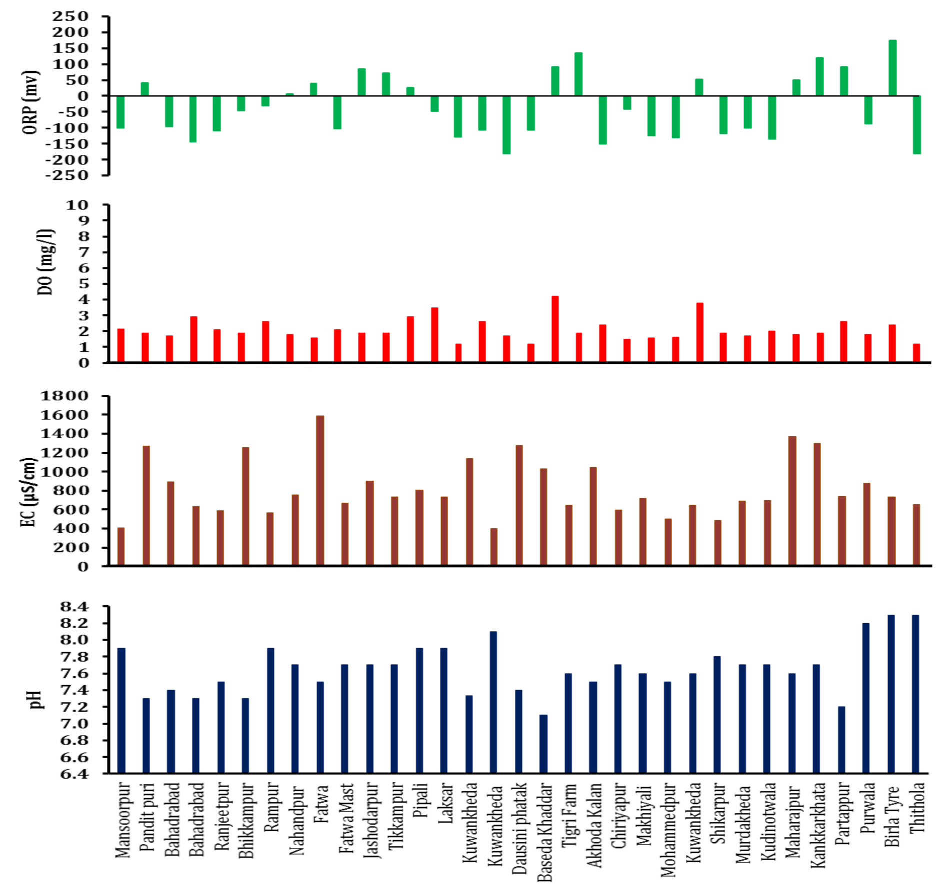

Fig. 2: Spatial variation in pH, EC, DO and ORP in groundwater samples of the study area

in Ganga and Solani rivers are 5 mg/l and 18 mg/l respectively. Results suggest that 57.6% of samples are within acceptable limit while 42.4 % samples exceeds the acceptable limit but within permissible limit for drinking water prescribed by BIS (2012). The weathering of Na and K silicate minerals like albite, anorthite, orthoclase and microcline are the major source of the Na and K in the aquatic system. In the study area, sodium is least abundant among the cations. Sodium concentration in the groundwater samples ranges from 7 mg/l to a maximum of 84 mg/l with an average concentration value of 24 mg/l, whereas in Ganga and Solani rivers, concentration of Na was observed as 4 and 15 mg/l respectively. The concentration of potassium in groundwater samples ranges between 9 mg/l and 98 mg/l with an average value of 25 mg/l whereas in Ganga and Solani rivers, concentration of K^+ was observed as 11 and 15 mg/l respectively.

concentrations of SO_4^{2-} in Ganga and Solani rivers are same and observed to be 5.0 mg/l. The sulphate concentrations are within the acceptable limit as prescribed by BIS, 2012. In the study area, concentration of nitrate in groundwater samples ranges from 0.8 mg/l to 56 mg/l with the average concentration value of 8 mg/l, whereas in Ganga and Solani rivers, nitrate concentration was measured as 0.4 and 8.8 mg/l respectively. The nitrate concentrations of all the analysed samples are within the prescribed drinking water limit of 45 mg/l except one sample (56 mg/l) collected from Purwala village. Fluoride is generally found in all natural waters at some concentration. In groundwater, however, low or high concentrations of fluoride can occur, depending on the nature of the rocks and the occurrence of fluoride-bearing minerals. Fluoride occurs as fluorspar (fluorite), rock phosphate, graphite, phosphorite minerals etc. in nature. Concentration of fluoride in groundwater samples varies between BDL and 1 mg/l and average concentration was found as 0.4 mg/l, whereas in Ganga river and Solani river concentration of F^- is 0.2 and 0.3 mg/l respectively. Concentration of fluoride is well within the acceptable limit of 1 mg/l.

Table 1: Chemical Characteristics of groundwater of the study area

Parameters	Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	Cl^-	SO_4^{2-}	F^-	NO_3^-	As	Fe	Mn
Min	7	9	24	10	144	8	2	ND	0.8	ND	30	2
Max	84	98	128	49	390	144	115	1.0	56	84	8730	3820
Avg.	24	25	54	29	231	44	37	0.4	8.0	13	2091	456
BIS Acceptable limit	-	-	75	30	-	250	200	1.0	45	10	300	100
BIS Permissible limit	-	-	200	75	-	1000	400	1.5	NR	50	NR	300

Units in µg/l

Bicarbonate may be derived from the dissolution of carbonates and/or silicate minerals by the carbonic acid. The HCO_3^- concentration in ground water samples varies from 144 mg/l to 390 mg/l (avg. 231 mg/l), whereas concentration of bicarbonate in Ganga and Solani rivers are 88 mg/l and 176 mg/l respectively. The Cl^- concentration in the groundwater samples varies between 8 mg/l to 144 mg/l (avg. 44 mg/l) whereas concentration of chloride in Ganga and Solani rivers are 4 and 32 mg/l respectively. The chloride concentrations are within the acceptable limit as prescribed by BIS, 2012. The chloride in ground water is primarily either from atmospheric source, sea water contamination or from anthropogenic sources. Abnormal concentration of chloride may result from pollution by sewage wastes. The sulphate is usually derived from the oxidative weathering of sulphide bearing minerals like pyrite, gypsum or anhydrite. SO_4^{2-} concentration of analysed groundwater samples in the study area varies between 2 mg/l to 115 mg/l (avg. 37 mg/l), whereas

Classification of water based on Piper diagram

Hydro-geochemical evolution of ground water depends on water-aquifer matrix interaction, ground water residence time within the aquifer and the associated chemical process during recharge e.g. cation exchange (Drever, 1997). The studied ground water from older and younger alluvium plain in the study area shows a distinct relationship with major solutes in the ground water. The Piper diagram (Fig.3) suggests that hydro-geochemical facies of groundwater of study area can broadly be classified into Ca–Mg-HCO_3 type.

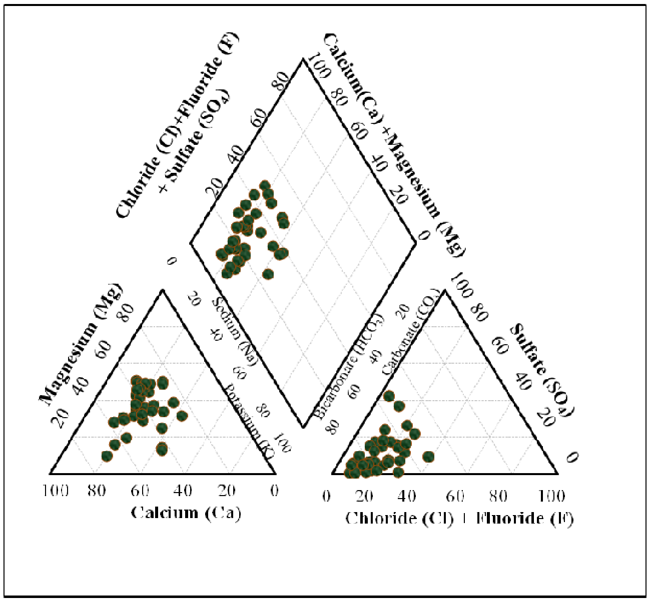

Fig. 3: Piper diagram of ground water samples of the study area

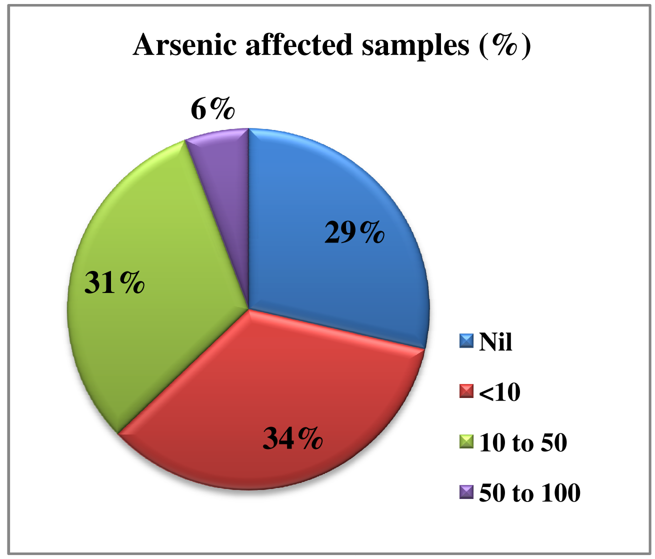

Fig. 4: Pi-diagram showing % of ground water samples affected with As (in ppb)

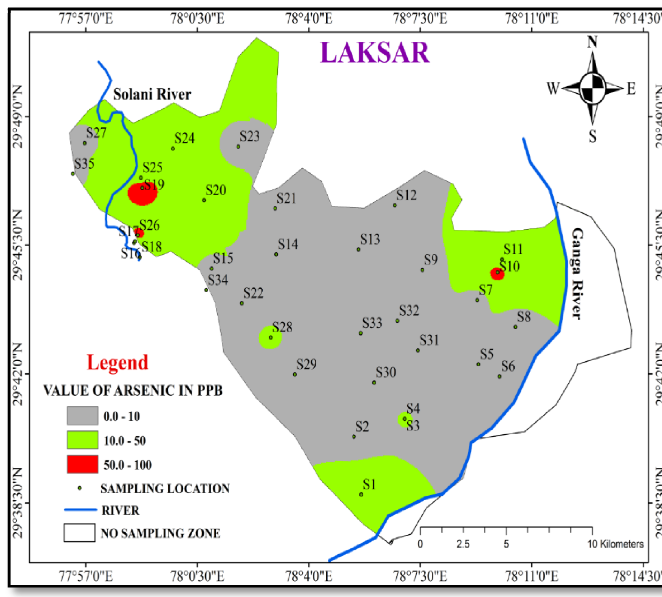

Fig. 5: Arsenic distribution map of the study area.

Arsenic Detection and Distribution

Heavy metals such as arsenic in ground water have a considerable significance due to their toxicity and adsorption behavior. The results of the analysed samples suggest that almost 63% of analysed samples are within the acceptable limit (10 µg/L) as per BIS (2012). Figure 4 shows approximately ~37% of water samples collected from the study area are enriched with As concentrations (>10 µg/L). Arsenic concentration ranges from below detectable limit (BDL) to 84 µg/L (average 13 µg/L). Ground water with elevated As (>50 µg/L) concentration is only present at two locations viz. Fatwa Village (63 µg/L) and Dausni Railway Fatak (84 µg/L) of Laksar area. In the present study, all the collected ground water samples are of shallow depth (private hand pump and govt. hand pump (depth 30 to 150 ft). Total As concentrations is present in the ground water of study area and higher concentration (> 50 ppb) is noted in the flood plain of Ganga and Solani rivers. The spatial distribution map of arsenic is shown in Fig. 5 which is prepared based on the point data. However, arsenic distribution may not be uniform in the study area as shown in Fig. 5. The concentration of iron in the ground water of the study area ranges from 30 to 8730 ppb with average concentration 2091 ppb. It is observed that 30% of the samples falling within the acceptable limit of 300 ppb and 70% of the samples exceeding the acceptable limit for drinking water purpose prescribed by BIS,2012. High concentration of iron may be attributed to the dissolution of iron bearing minerals from the soil strata.

The concentration of manganese ranges from 2 to 3820 ppb. It is observed that about 20% of the analysed samples fall within the acceptable limit of 100 ppb and 43% samples exceed the acceptable limit but falling within the permissible limit of 300 ppb whereas 37% of samples exceed the permissible limit.

Correlation of Arsenic with other solutes

Numerous previous studies in lower gangetic plain have described the relationships of As with other solutes (Biswas et al., 2014) and combined effects of HCO_3^- and pH in As mobilization from surface of Fe-Mn(OOH) and aquifer sediments. Lot of hypothesis have been given for the relationship between Fe and As, where many studies showed positive co-relationship (Dowling et al., 2002). Various studies revealed that correlations between As and other redox-sensitive parameters (e.g. Fe, Mn, SO_4, NO_3) may be limited by the occurrence of multiple reactions in heterogeneous sediments (Mukherjee and Fryar, 2008). In the present study, moderate correlation of As with Fe and Mn and a weak correlation with SO_4 and HCO_3 have been observed (Fig. 6). There is a need of detailed hydrogeological investigations to study the reason for occurrence of As in the area.

samples i.e. at two locations (namely Dausni Railway Fatak and Fatwa village) exceed the permissible limit (50 ppb) for the drinking purposes as prescribed by BIS, 2012. A moderate correlation of As with Fe and Mn and weak correlation with SO_4 and HCO_3 have been observed.

- The iron concentration ranges from 30 to 8730 ppb and ~70% samples exceeding the acceptable limit of 300 ppb for drinking water purpose as prescribed by BIS, 2012.

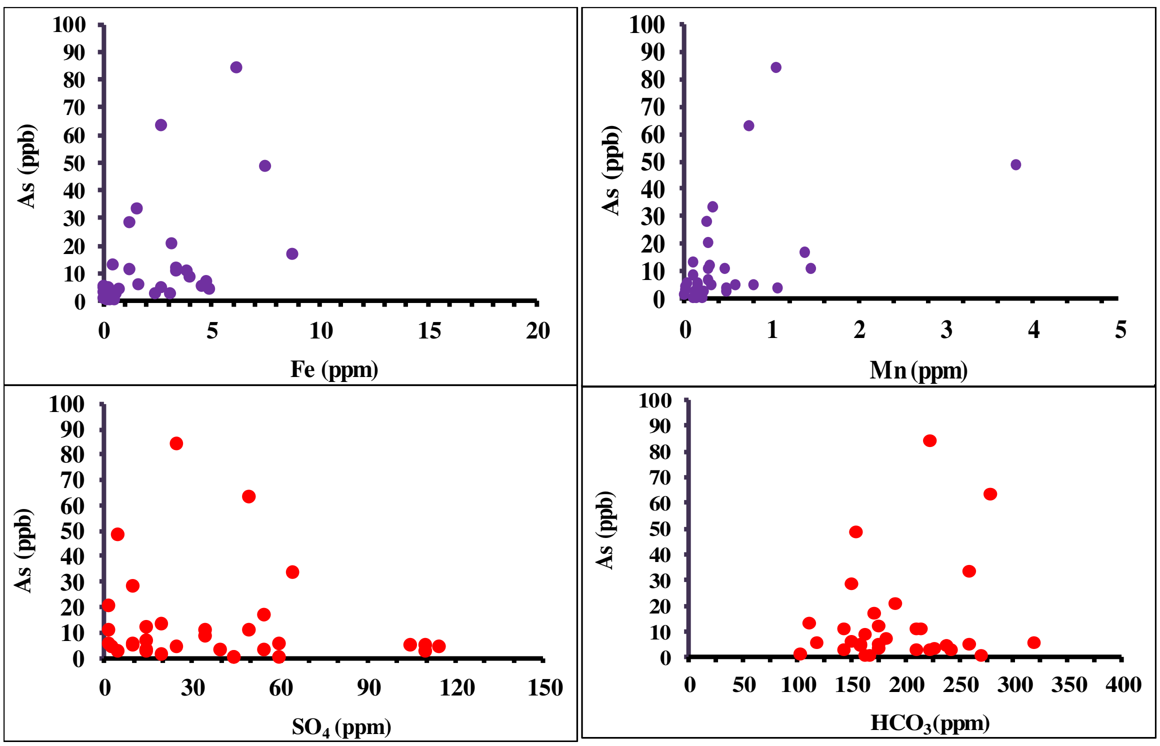

Fig. 6: Correlation of arsenic with other water quality parameters in ground water samples.

CONCLUSIONS

The following conclusions are drawn based on the present study:

- Arsenic concentrations in Laksar area of Haridwar district, Uttarakhand is reported for the first time based on the investigations carried out in the present study. Arsenic concentration ranges from below detectable limit (BDL) to 84.0 ppb. The enrichment was encountered in the sampling sites that are close to the flood plains of Solani and Ganga rivers. The samples which show As concentration more than 10 ppb generally tend to have negative ORP suggesting anoxic/anaerobic conditions in the aquifer.

- The arsenic concentration in ~37% samples exceeds the acceptable limit (10 ppb) and 6% of groundwater

- Calcium alone constitute 41 % of the total cations (TZ^{+}) and HCO_3 constitutes 75 % of the total anions (TZ^{-}) in groundwater of the area. The hydro-geochemical facie of groundwater is Ca-Mg- HCO_3 type.

- For better drinking management policy, government and other water supply and investigation department may target continuous monitoring of the arsenic affected area. A detailed hydro-geochemical and arsenic genesis study should be carried out.

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REFERENCES

1. APHA. (2012). Standard Methods for the Examination of Water & Wastewaters, American Public Health Association, 22th Edition, Washington DC.

2. BIS. (2012). Indian Standard-Drinking Water Specification (2nd Revision), IS 10500: 2012, Bureau of Indian Standards, New Delhi.

3. Biswas, A., Gustafsson, J. P., Neidhardt, H., Halder, D., Kundu, A. K., Chatterjee, D. & Bhattacharya, P. (2014). Role of competing ions in the mobilization of arsenic in groundwater of Bengal Basin: insight from surface complexation modeling. Water research, 55, 30-39.

4. CGWB. (2016). A report on Aquifer Mapping and Ground Water Management Plan, Haridwar district , Uttarakhand. Central Ground Water Board.

5. Dowling, C. B., Poreda, R. J., Basu, A. R., Peters, S. L., & Aggarwal, P. K. (2002). Geochemical study of arsenic release mechanisms in the Bengal Basin groundwater. Water Resources Research, 38(9), 12-1.

6. Drever, J.I. (1997). The Geochemistry of Natural Water: Surface and Groundwater Environments. 3rd Edition, Prentice Hall, New Jersey.

7. Kumar, M.; Ramanathan, A.; Rahman, M.M.; Naidu, R. (2016). Concentrations of inorganic arsenic in groundwater, agricultural soils and subsurface sediments from the middle Gangetic plain of Bihar, India. Sci. Total Environ., 573, 1103–1114.

8. Mukherjee, A., & Fryar, A. E. (2008). Deeper groundwater chemistry and geochemical modeling of the arsenic affected western Bengal basin, West Bengal, India. Applied Geochemistry, 23(4), 863-894.

9. Nickson, R.T., McArthur, J.M., Shrestha, B., Kyaw-Myint, T.O., Lowry, D. (2005). Arsenic and other drinking water quality issues, Muzaffargarh District, Pakistan. Appl. Geochem. 20, 55−68.

10. Ramanathan, A.L., Bhattacharya, P., Tripathi, P. (2006). Arsenic in ground water of the aquifers of central Gangetic plain of Uttar Pradesh, India. Geol. Soc. Am. Abstracts with Programs 38(7), 241.

11. Saha D., Sarangam S.S., Dwivedi S. N. and Bhartariya K. G. (2010). Evaluation of hydrogeochemical processes in arsenic contaminated alluvial aquifers in parts of Mid-Ganga Basin, Bihar, Eastern India. Environ. Earth Sci. 61, 799–811.

12. Singh, S. K., Ghosh, A. K., Kumar, A., Kislay, K., Kumar, C., Tiwari, R. R., & Imam, M. D. (2014). Groundwater arsenic contamination and associated health risks in Bihar, India. International Journal of Environmental Research, 8(1), 49-60.