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Isotope hydrological investigation in arsenic infested areas of West Bengal, India

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Abstract

The presence of arsenic in groundwater is an environmental problem of considerable importance. About a million people living over an area of 37,000 km^2 in West Bengal, which is located in Indo-Gangetic plain, consume arsenic laced drinking water. In this area, arsenic levels in groundwater have been found to be 0.01 mg/L to 3.0 mg/L. Environmental isotope techniques have been applied to study the origin, source, residence time and the dynamics of arsenic contaminated and uncontaminated aquifers in Murshidabad, Nadia and North and South 24-Parganas districts in West Bengal. Groundwater samples from different depth and a few surface water samples have been collected, during post and pre-monsoon period in 1996 - 1999 and analysed for ^{2}H, ^{18}O, ^{13}C, ^{34}S, ^{3}H and ^{14}C isotopes as well as arsenic concentration. Results show high arsenic content (0.01 to 1.3 mg/L) in shallow aquifer (Depth: <100m) compared with deep aquifer in Murshidabad and Nadia districts. stable isotopic ($\delta^{2}H$ and $\delta^{18}O$) contents of these groundwaters show contribution of local precipitation as well as river water. They have modern tritium and carbon -14 content. In deep aquifer (Depth: >100m), arsenic concentration is within the permissible limit and their stable isotope, tritium and carbon-14 contents indicate possible interconnection between shallow and deep aquifer.

In North and South 24-Parganas districts, shallow aquifer shows very high arsenic (0.01 to 3.0 mg/L) concentration. In South 24 - Parganas, shallow groundwaters are more depleted in stable isotopic content($\delta^{2}H$ &$\delta^{18}O$) compared with deep groundwaters. In both cases, tritium and carbon - 14 values of the shallow groundwaters indicate the precipitation input, and possibly they are a mixture of young and old groundwater. In deep aquifer, arsenic is within the permissible limit. They have low tritium and carbon -14 contents indicating that they are old waters.

The overall isotope hydrological studies indicate that in Mursidabad and Nadia districts, there is a possibility of interconnection between shallow and deep aquifers and receive recharge from River Ganga as well as local precipitation. Surface and deep groundwaters are free from arsenic. Over-exploitation of shallow aquifer may make deep aquifer also vulnerable to arsenic contamination. In North and South 24-Parganas districts, the chances of interconnection between shallow and deep aquifers are remote. Shallow aquifer is a mixture of old and young water, whereas deep aquifer is old water. The elevated arsenic concentration in groundwaters of Murshidabad, Nadia, and North and South 24 Parganas is possibly released from the sediment under anoxic condition in the aquifer.

INTRODUCTION

Arsenic has been known in India for millennia, as an ingredient in Ayurvedic medicines, and in crime (legends of “Vishakanya”, and murders). It was believed that intake of arse-

nic improved complexion. Arsenic occurs in the environment in four states of oxidation (+5, +3, 0 and -3). As^{5+}(arsenate) occurs in waters at high Eh values and oxygenated systems, while As^{3+}(arsenite) occurs at lower Eh values and mildly reducing conditions. Arsenite has greater mobility in both sediment and water than arsenate. As^{0} and As^{3-} are rare in aquatic environments. Arsenic is toxic to both plants and animals, and its trivalent form is considered to be much more toxic than pentavalent form. Arsenic has been categorized as a class 'A' carcinogen by United States Environmental Protection Agency (USEPA). The permissible limit of arsenic in drinking water is now 0.01mg/L though for all practical purposes a limit of 0.05 mg/L is normally quoted. If it exceeds the threshold limit in drinking water, then the arsenic toxicity can cause hyperkeratosis, 'blackfoot' disease, myocardial ischemia, liver, lung, kidney and skin cancer. Arsenic contamination episodes in drinking water have been reported from many places such as Taiwan, Chile, Bangladesh, New Hampshire, Southern region of Japan, Zimapan valley of Mexico, southwestern France and various parts of USA such as Arizona, California, Montana, Nevada, Oklhoma and Washington.

In India, arsenic laced drinking water is being consumed by about a million people living over an area of about 37,000 km^2 in six districts of West Bengal, which is located in the Indo-Gangetic plain. About a million people are already suffering from arsenic related diseases. High arsenic (0.01 to 2.8 mg/L) in the groundwater has been encountered in Murshidabad, Nadia, Malda, Burdhwan and North and South 24-Parganas districts (Fig. 2) The mid-1970s saw a large scale exploitation of groundwater resources for irrigation purposes as a consequence of exodus of 80 - 90 million people from Bangladesh to the border districts of West Bengal. Adverse health effects due to the consumption of groundwater with excess arsenic content manifested in the population within the time span of 8 - 10 years.

The source of arsenic in groundwater as well as in surface water is mostly from leaching of geological material, input from geothermal sources, mining wastes and landfills. Uncontrolled anthropogenic activities such as smelting of metal ores, use of arsenical pesticides and wood preservative agents may release arsenic directly to the environment. Occurrence of arsenic in natural water depends on local geology, hydrology and geochemical characteristics of aquifer materials. Furthermore organic contents in sediments as well as land use pattern may also be important factors controlling the natural mobility of arsenic in the aquifers (Bhattacharya et.al, 1997)

Inspite of the reported occurrence of high arsenic in groundwater of West Bengal, the people of the area are solely dependent on the groundwater resources in the region. Research carried out so far concerned quantitative determination of the level of arsenic in groundwater and epidemiological studies among the population in the infested zones. Geochemical investigations pertaining to the occurrence of arsenic in groundwater in West Bengal are also being carried out to evaluate overall quality of groundwater and the geochemical processes that control groundwater chemistry. The examination of the geohydrological conditions is essential to understand the impact of groundwater development, on arsenic levels. The most useful environmental isotopes in groundwater pollution studies are ^{2}H, ^{18}O, ^{34}S, ^{13}C, ^{15}N, ^{11}B ^{3}H and ^{14}C. It is essential to integrate isotope techniques along with conventional hydrogeology and hydrochemistry. Again trace elements

have an important role to play in an integrated approach for the interpretation of contaminant source and pathways.

In West Bengal, arsenic infested areas are covered by unconsolidated allocthonous sediment. Interaction of arsenic bearing sediment with groundwater under different subsurface environmental conditions plays an important role in controlling retention and mobility of arsenic in this delta region. Identification of key processes leading to the release of arsenic to groundwater would help in evolving suitable remediation procedures. Therefore, isotope geochemical techniques have been applied to understand the possible mechanism responsible for retention/mobility of arsenic in groundwater under prevailing hydrodynamics of the arsenic contaminated aquifers and to identify the provenance of the arsenious sediment and also to examine the various options for remedial measures to overcome the problem.

GEOLOGY

Three fourths of the Bengal basin is covered by alluvial deposits and the rest is covered by hard rocks (Fig. 1). Western part of the basin is covered by Peninsular Shield with inter-cratonic Gondwana basin and Rajmahal trap, Shillong plateau on the Northeast, and Naga Lushai belt in the East. The Garo-Rajmahal gap separates the Peninsular Shield from the Shillong Plateau. The gap is created due to tectonic movement. The sedimentary fill occurring north of the Garo-Rajmahal gap perhaps represents a part of crystal downwarp during the Himalayan Orogeny.

In the Bengal basin, the upper delta is covered by Quaternary sediment. It is fluvitile in nature and primarily formed by alluvial sediment transported by river Damodar, Mayurakshi, Ajoy, etc., from Chota-Nagpur upland in the West and also rivers flowing from Himalayas such as the Ganga, Bramhaputra and their distributaries. Arsenic contaminated groundwater occurs in this sediment and extends eastwards in the Bengal basin and beyond in Bangladesh (Nickson, et al, 1998). This delta is characterised by a series of abandoned river channels formed under varying hydrodynamic conditions in a fluvial regime. Abandoned meandering scrolls are the most common form and could be related to flood plain formation. The sediment of this plain consists of several sequences of clay, sand, silt and conglomerate.

The lower delta consists of tidal mud, distributor levees and interdistributory marshy complex formed under a fluvial estuarine and marine environment under the influence of fluctuating sea level in Tertiary and Quaternary. This plain is characterised by the presence of extensive clay blankets which is underlain by silt, sand and gravel. Most of the arsenic affected areas are located in the upper deltaic plains and southeastern part of lower delta. In this region, arsenic concentration is high in fine sand and clay bed. Core samples collected from Birohi exploratory well, Nadia district have been analysed for arsenic as well as mineralogy. Arsenic bearing sediment is cogenetic and arsenic concentration is higher in clay (0.3 to 1.8 mg/l) than in sand (< 0.2 mg/L). This suggests that arsenic is drained to the Bengal basin from an outside source and later it was adsorbed or

CO-precipitated with fine sediment at the time of sedimentation. The source of arsenic may be from eastern parts of Bihar or the metamorphic terrain of Himalayas.

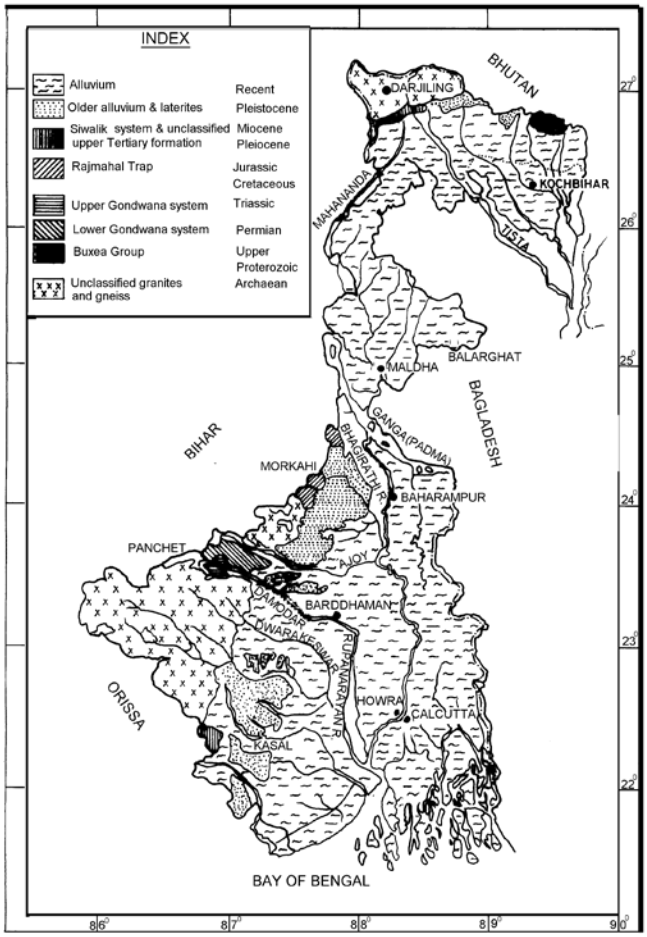

Figure 1. Geological map of West Bengal.

HYDROGEOLOGY

The upper delta region of the Bengal basin, is characterized by unconfined aquifers of Quaternary. These aquifers are gradually merged into semi-confined /confined state as they extend towards south. Finally in the lower delta, the most important aquifers are in early Quaternary sediments under clay blanket. In the western part of the Bengal basin groundwater occurs in both unconfined and confined condition.

In the upper delta (Malda, Murshidabad, Nadia and Burdhwan), groundwater occurs in unconfined /semi-confined condition and the water level varies from 4 to 9 m below ground level. In the Eastern part of the basin, groundwater fluctuation is in the range of 0-3 m (Chakraborty, et al. 1994).The general trend of groundwater flow in the upper

delta is North to South and Southeast direction in the lower delta. In lower delta, groundwater occurs under unconfined/semi-confined condition. Depth to the water level for shallow aquifer varies from 3-5m and for semi-confined aquifer 6.-8 m below ground level. Groundwater flow is mostly towards southeast (Shivanna, et al., 1999).

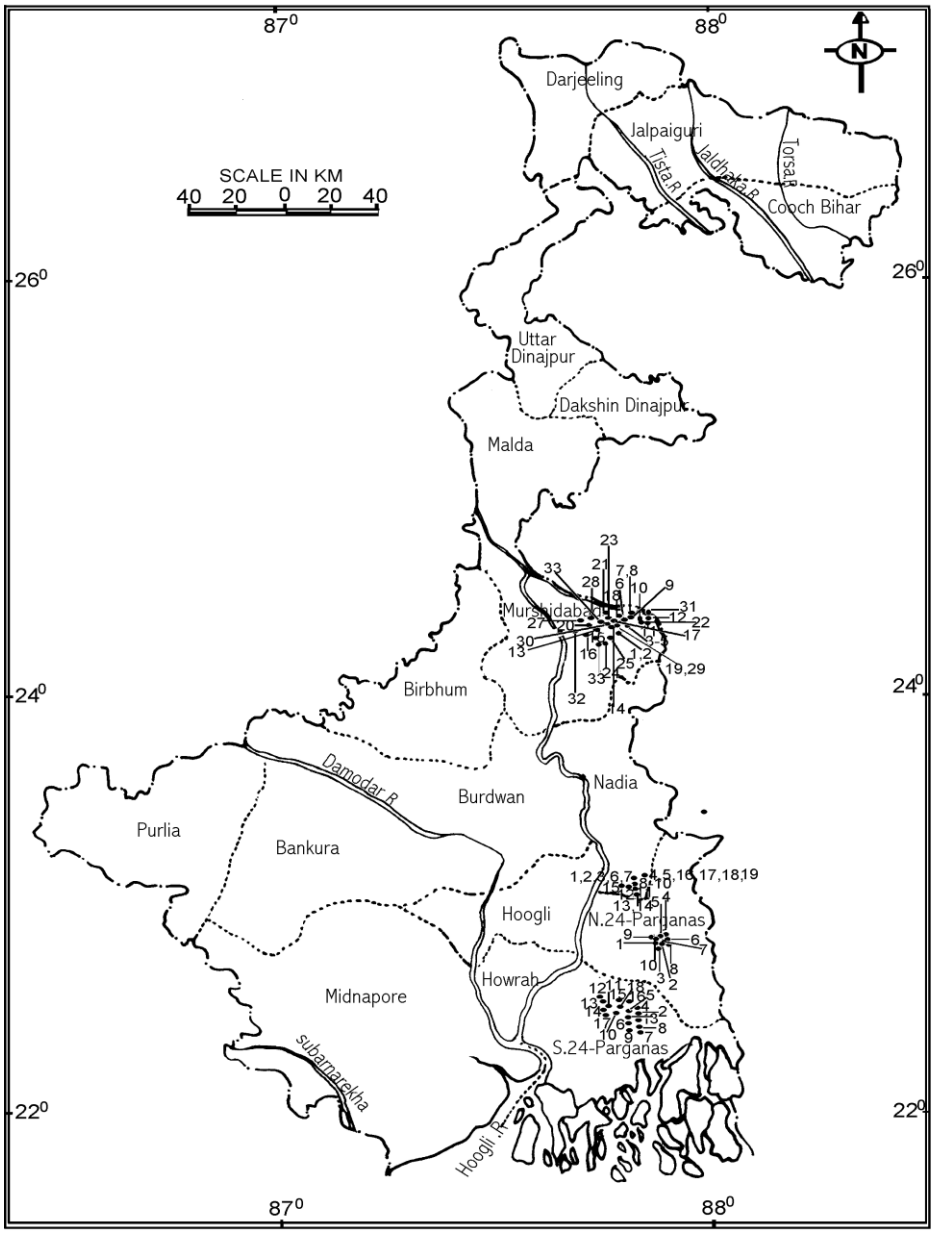

Figure 2. Sample location map.

HYDROCHEMISTRY

Water samples collected from Murshidabad, Nadia and North and South 24-Parganas were analysed for major ion chemistry in Central Ground Water Board, Calcutta and arsenic analysis were carried out in Bhabha Atomic Research Centre, Mumbai. Sample locations are given in Fig. 2. The hydrochemical data of Murshidabad and Nadia reveals that arsenic concentration exceeds permissible limit In Raninagar block-I and II as well as in Domkal block of Murshidabad district arsenic content is in the range of 001 - - 0.9 mg/L. Whereas in Chakdha block (Ghoraghata and Mandalhat) of Nadia district it is in the range of 0.01 - 1.3 mg/L. The high concentration of arsenic has been observed between 10 m to 100m below ground level (Fig. 3) In both the districts, surface and deep groundwaters arsenic concentration is within the permissible limit(< 0.01 mg/L). Both shallow and deep aquifers are fresh (Chloride: 18 to 96 mg/L) and their pH values are in the range of 6.9 to 7.4. Iron content is high in arsenic contaminated groundwaters and it is in the range of 0.1 to 7.0 mg/L and dissolved oxygen 0 to 5.0 mg/L. These waters are of Ca-Mg-HCO_3 type. Hydrochemical facies in these groundwaters change from HCO_3 $\rightarrow$ HCO_3 + Cl $\rightarrow$ Cl +HCO_3. The low content of sulphate in these groundwaters possibly explains the absence of SO_4+HCO_3 and SO_4+Cl facies.

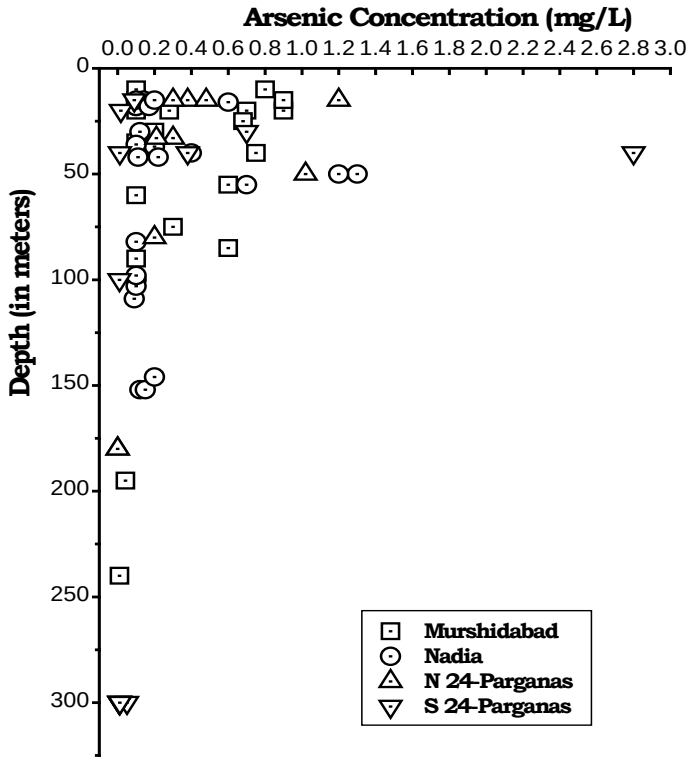

Figure 3. Arsenic Vs Depth profile.

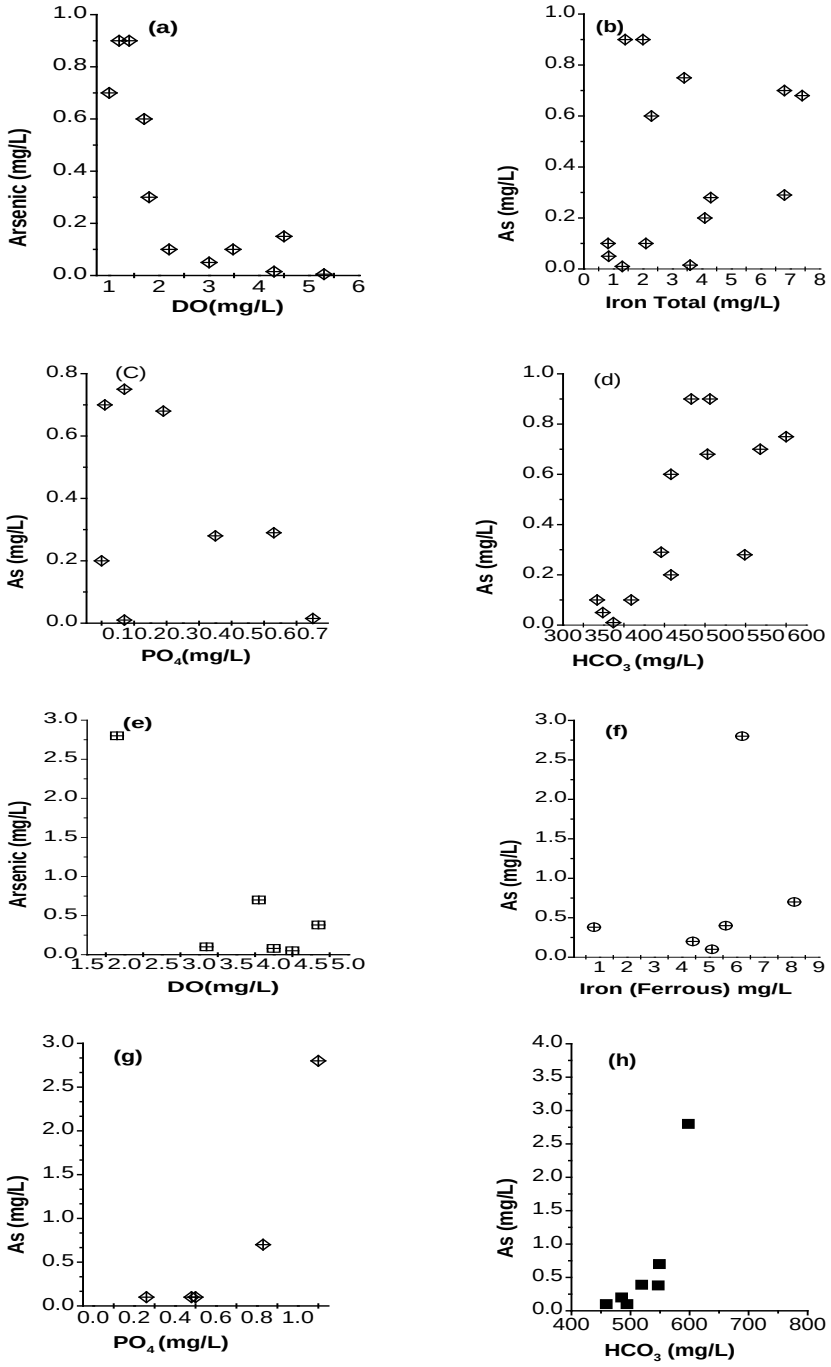

Figure 4. As Vs D.O, Fe, PO_4 & HCO_3 of Murshidabad (a, b, c & d) and South 24 -Pargnas (e, f, g & h)districts.

In North and South 24-Pargnas district, arsenic levels are high. In South 24- Pargnas district, the highest arsenic concentration observed in shallow ground waters of Gaptal (0.7 mg/L) and Paschim Mallipur (2.8mg/L) in Ramnagar and Baruipur blocks and in North Pargnas, North Kolsur (1.2 mg/L), Nithaipad (1.02mg/L). Groundwaters are of Ca-HCO_3 type and at a few places water is Na - HCO_3 type. Their pH values are in the range of 6.6 to 7.5, dissolved oxygen content varies from 0.0 to 7.0 mg/L and total iron content is in the range of 1.0 to 8.0 mg/L.

The overall hydrochemical results indicate that the arsenic contaminated groundwaters in Murshidabad, Nadia and North and South 24 - Parganas districts are generally mild acidic to alkaline in nature. High arsenic (shallow groundwaters: < 100m depth below ground level) is associated with high bicarbonate, iron and low sulphate, chloride and dissolved oxygen (see Figures 4).

ISOTOPE STUDIES

About 200 groundwater samples from different depths as well as surface water and rain water from Murshidabad, and South 24- Parganas districts were collected during December 1996, May 97, January 98 and June and December 99 for environmental isotope ^{2}H, ^{18}O, ^{3}H, ^{13}C, ^{14}C analyses and a few samples for ^{34}S measurement. Sample locations are shown in the Figures 2. Selected samples were measured for $\delta^{2}H$, $\delta^{18}O$, $\delta^{13}C$, ^{3}H and ^{14}C in Bhabha Atomic Research Center and $\delta^{34}S$ in Atomic Minerals Division, Hyderabad. The results obtained have been summarized below.

Surface water

A few surface water samples (River Padma, Bhagirathi and Ratnakar) were analysed for $\delta^{2}H$, $\delta^{18}O$ and ^{3}H. The results obtained during Dec. 96 and May 97 have been compared and the results show there is seasonal variation in $\delta^{2}H$ and $\delta^{18}O$. Post monsoon samples show more depleted values ($\delta^{18}O$:-8.6‰ to -5.15‰) compared to pre-monsoon samples (-6.7‰ to -3.5 ‰). The enrichment in May `97 samples is because of greater evaporation of the river water during summer. The tritium values of the river for post monsoon (5. 6 to 11.9TU) and pre-monsoon (7.0 to 10.3 TU) are nearly the same. Arsenic level in the river water have been found to be negligible.

Groundwater samples

M**urshidabad and Nadia:** In Murshidabad district shallow groundwater $\delta^{2}H$ and $\delta^{-18}O$ values respectively are in the range of -46.0‰ to -24.0‰ and -8.0 to –3.0 ‰ during Dec.`96 and -41.0 ‰ to -20.0 and -7.5 ‰ to -3.0‰ during May`97. These samples fall on meteoric line on $\delta^{2}H$ - $\delta^{18}O$ plot (Fig.5). Stable isotope results of the shallow groundwaters indicate that the recharge to shallow aquifer could be due to precipitation input. Some samples show depleted stable isotopic values during May`97 (Bichapad $\delta^{18}O$:-7.5‰, Raninagar $\delta^{18}O$:-6.9‰) indicating some river input. Stable isotopic composition of shallow, intermediate and deep groundwaters show similar $\delta^{18}O$ values (~ -6.0‰) showing possible interconnection. The tritium values of shallow groundwater generally have values in the range 2 to 10 TU showing that they are due to modern recharge. Higher tritium values observed in Lalbagh shallow tube well (STW), 10 TU,

Chunakati Nimtala STW 10 TU, Debipur STW 11 TU, Bichapad STW 9 TU and Gosak-para could be due to recharge from the rivers.

A few shallow groundwater samples were measured for $\delta^{13}C$ and their values are in the range of -6.0 to -18.0‰ indicating oxidation of organic matter in the aquifer. Carbon-14 values of the shallow groundwaters are in the range of 87 to 109 pMC indicating that they represent mostly modern recharge (< 50 years). The deep groundwater samples from Murshidabad have tritium values < 2 TU. Carbon-14 values are in the range of 78 to 85 pMC showing that they are older compared to shallow zone waters

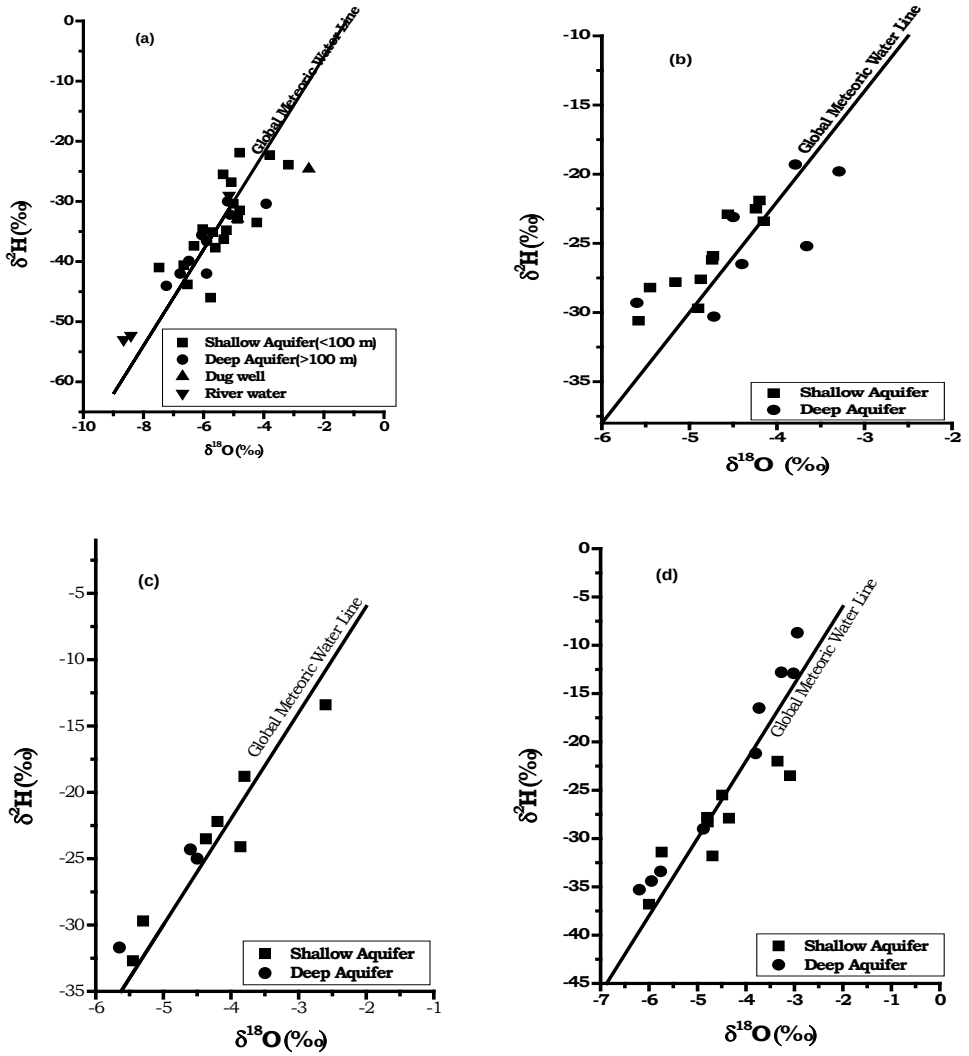

Figure 5. Deuterium - Oxygen Plot: (a) Murshidabad, (b) Nadia, (c) North 24-Pargnas and (d) South 24 Pargnas.

Shallow groundwaters of Nadia district show stable isotopic content, δ^2H: -27.0 to -21.0‰ and $\delta^{18}O$:-5.5 to -3.1‰ and their ^3H values are in the range of 1.5 to 9.0 TU. Only two shallow groundwater samples were measured for carbon-14 and their values 75 and 84 pMC respectively. In this area, deep groundwater stable isotope (δ^2H &$\delta^{18}O$) as well as radioisotope (^3H & ^{14}C)values are similar to that of shallow groundwaters indicating the possibility of interconnection between shallow and deep aquifers.

North and South 24 Pargnas: North 24- Pargnas shallow groundwaters are slightly enriched in stable isotopic content (δ^2H; -32.7‰ to -13.4‰ and $\delta^{18}O$: -4.4 ‰ to -2.6‰) compared with deep groundwaters (δ^2H : -31.7‰ to -24.4‰ and -5.6‰ to -4.5‰). Their tritium content is in the range of 5.0 to 9.0 TU. Whereas in deep groundwater tritium content is almost negligible (<1.0 TR) and they are old waters. The enrichment of stable isotope content in shallow groundwater is mostly due to local precipitation recharge as well as the influence of sea.

In South 24 -Pargnas district, shallow groundwaters are slightly depleted in δ^2H and $\delta^{18}O$ compared to deep groundwaters. Shallow groundwater δ^2H and $\delta^{18}O$ values range from -37.0 ‰ to -22‰ and - 6.0‰ to -3.5‰ respectively and deep groundwater values are in the range of -9.0 ‰ to -16‰ and -6.0 ‰ to -3.0‰. They fall in two different groups on δ^2H and $\delta^{18}O$ plot indicating that shallow and deep groundwaters are not interconnected (Fig. 8). Only two shallow groundwater samples were measured for $\delta^{13}C$ and their values are -3.2 & -4.1‰. The enriched $\delta^{13}C$ values could possibly be due to inorganic oxidation in the system. The tritium values of the shallow groundwater range from 0.8 to 1.7 TU and the deep groundwater range from 0.5 to 0.8 TU. Carbon -14 values of shallow groundwaters range from 84 to 85 pMC and deep groundwater rang from 20 pMC to 22 pMC. Deep groundwater ^{14}C data has been corrected using Pearson`s model and model age is in the range of 5000 years BP to 13000 years BP. Based on ^{14}C results, two old groundwater pockets are identified in this district. One is in Baruipur area (about 13,000 years BP) and second one is in Ramnagar area (about 5000 to 6000 years BP).

$\delta^{34}S$ values of the aqueous sulphate are measured for 8 shallow groundwaters collected from Murshidabad and South 24 - Pargnas districts. The values are in the range of+3.2‰ to +15.0‰. It could be seen from table -1 groundwaters containing low sulphates show enrichment in $\delta^{34}S$. This suggests that the observed $\delta^{34}S$ enrichment is bacteriogenic. This is also confirmed by the presence of hydrogen sulphide in the waters.

Table 1. $\delta^{34}S$ Results (Murshidabad and South 24 - Pargnas Districts).

S.No.	Location	Depth (m)	As (mg/L)	SO_4 (mg/L)	$\delta^{34}S$ (‰)
1.	Tejsinghpur	20	0.9	14	+4.4
2.	Katlamari	20	0.7	05	+4.6
3.	Herampur	15	0.9	12	+7.6
4.	Moktapur	55	0.6	1.2	15.6
5.	Suparigola	30	0.015	130	+3.2
6.	Ramnagar	40	0.38	2.5	+5.5
7.	Dhap Dhabi	40	2.8	1.6	+3.7
8.	Baruipur	20	0.39	5.7	+5.3

S.No. 1 to 5 from Murshidabad district & 6 - 8 from South 24 - Pargnas Dist**.**

DISCUSSION AND CONCLUSION

In Murshidabad and Nadia districts, shallow and deep groundwaters are interconnected whereas in North and South 24 -Pargnas districts, the chances of interconnection between shallow and deep aquifer are remote. Even though arsenic concentrations in shallow groundwaters of these two districts are high (0.01 to 2.8 mg/L), the spatial distribution of arsenic concentrations mainly depends on the nature of sediment, groundwater flow condition and geochemical conditions. The hydrochemical results of the arsenic infested areas of these districts show that much of the arsenic is in younger alluvium east of Bhagirathi river. In the western and south western parts, arsenic concentrations are within the permissible limit. Most likely the arsenic which is in the parent rock might have separated due to weathering and drained towards Bengal basin. At the time of sedimentation, arsenic might have CO-precipitated/adsorbed on fine sand and clay along with iron oxide. The elevated arsenic concentration in shallow groundwaters is possibly due its release, when arsenic rich iron oxyhydroxides are reduced in anoxic environment in the aquifer. Subsequently, concentration of iron, manganese, bicarbonate and phosphate contents are elevated in the groundwater (see Figure 4). In Murshidabad and Nadia districts, since shallow and deep aquifers are interconnected, deep aquifer is vulnerable to arsenic contamination. In North and South 24- Pargnas district, since the shallow and deep aquifers are not interconnected, the chances of deep aquifer getting contaminated with arsenic from shallow aquifer are remote.

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