

# Scinario of arsenic pollution in groundwater: West Bengal

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**Abstract:** Arsenic contamination in groundwater has taken a serious stage and it has entered the food chain now. Rice and other vegetables grown using arsenic contaminated groundwater are accumulating arsenic in levels greater than prescribed limit for health. Although several remedial solutions have been suggested, considering the socio-economic condition of the agrarian population, it is recommended to use surface water for irrigation. It may be difficult to switch over to this practice but there seems to be no other economical option suitable for this population. Over a period of years, the aquifer may provide safe drinking water and reduce the severity of the health condition presently experienced by the population.

**Key Words:** arsenic poisoning, West Bengal, bioaccumulation of arsenic, arsenic and tube wells

**CLC number:** X143    **Article Character:** A    **Artical ID:** 1000-3657(2010)03-0712-10

## 1 Introduction

It is well known that geogenic arsenic contamination in groundwater in West Bengal has become a global problem and numerous publications have documented the concentration and the biological effects of As on humans <sup>[1-20]</sup>. About 44% of total population of West Bengal is suffering from arsenic related diseases like conjunctivitis, melanosis, hyperkeratosis, and hyper pigmentation. In certain areas gangrene in the limb, malignant neoplasm and even skin cancer have also been observed. It has been reported that dermatitis affects nearly 7.19 % of population in the age group of 1-19 years. Children below 11 years age with poor nutrition easily get affected by arsenic related diseases <sup>[21]</sup>. In West Bengal groundwater the arsenic varies from 0.05 to 3.7 mg/L, with an average of 0.2 mg/L while the arsenic limit in recommended drinking water is 10  $\mu$ g/L <sup>[22]</sup>. Recently arsenic uptake by food crops like rice and wheat in

West Bengal has also been documented <sup>[4,23]</sup>. High levels of arsenic in rice is also reported from Bangladesh <sup>[24]</sup>. It is quite apparent now that arsenic, besides groundwater has entered the food chain. Recent reports indicate high arsenic content in groundwater from other states like Bihar, Assam, Tripura, Arunachal Pradesh and Nagaland <sup>[25,3]</sup>.

## 2 Arsenic content in groundwater of west Bengal, Bihar and NE areas

West Bengal is one of the states severely affected by naturally occurring inorganic arsenic in groundwater. Murshidabad, Malda, Nadia, North 24 Parganas, South 24 Parganas, Bardhaman, Howrah, Hoogly and Kolkata are the nine districts affected by arsenic poisoning. About 50 million people living in 3200 villages are severally affected by arsenic related diseases. The concentration of arsenic in these nine districts is shown in figure 1 and the range of arsenic in the groundwater of the above states is given in table

1 and the arsenic content in certain parts of the human body is given in table 2.

3 Sources and behavior of arsenic in groundwater

Natural geological sources of arsenic are rock-forming minerals and arsenic ore minerals. The distribution of arsenic among co-existing minerals within the same rock has been documented [26,27]. Magnetite and ilmenite show relatively high concentration of arsenic. Arsenic in sulfide does not appreciably contribute to a whole rock. In rock forming minerals, arsenic (ionic radii  $As^{3+}$  0.58 and  $As^{5+}$  0.56 Å<sup>0</sup>) can probably substitute for  $Si^{4+}$  (0.43),  $Al^{3+}$  (0.51),  $Fe^{3+}$  (0.64) and  $Ti^{4+}$  (0.68 Å<sup>0</sup>). Arsenic occurs as an element, arsenides, sulfides, sulfosalts (complex

sulfides), oxides, numerous arsenates and a few arsenites in some minerals, where it occurs as major constituent. Arsenopyrite and realgar are main arsenic sources. Arsenic content in various rock types and minerals is given in table 3.

Besides the above listed naturally occurring minerals, high arsenic content in coal is also reported from NE India (Table 4). Thus coal and coal ash are also potential sources for arsenic in groundwater. Indian coal contains 3.72 % of arsenic and a large amount of this arsenic enters the ash. The ash generated by coal plants in India is about 250-400 kg/ton of coal [3]. The exact amount of arsenic contributed by coal ash to groundwater is yet to be established.

The arsenic released to the environment ultimately enters the human body through drinking water. Arsenic is perhaps unique among oxianion-forming elements (e.g. antimony, molybdenum) in its sensitivity to mobilization under oxidation and

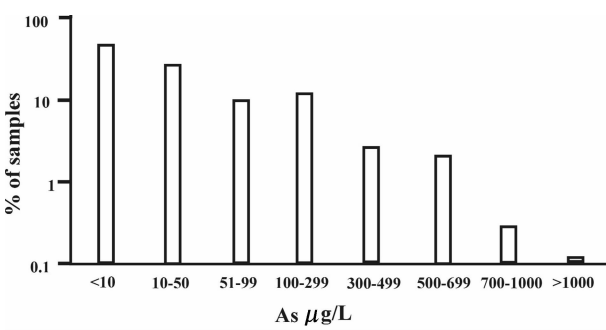


Fig.1 Arsenic concentration in the nine districts of West Bengal (Modified after[3])

Table 1 The concentration of arsenic in groundwater from West Bengal, Bihar and NE states(modified from [3, 25])

Location	Well depth/m	As/(g/L)
West Begal	1-305	<1-1300
Bihar	NA	<10 -1000
Assam	NA	19 - 986
Arunachal Pradesh	NA	58 - 618
Tripura	NA	50 - 444
Nagaland	NA	50 - 278

Table 2 Arsenic content (µ g/kg) in certain human parts in West Bengal population (modified from[3])

	Urine	Hair	Nails	Skin-scale
Max	3147	20340	44890	1550
Min	10	180	380	1280

Table 3 Arsenic content in certain geological material (modified from[28])

Rock/Mineral	Arsenic/10 <sup>-6</sup>
Ultrabasic rocks	0.03-15.8
Basic rocks	0.18-113
Acidic rocks	0.2-15
Schists	0.01-18.5
Sandstone	0.06-120
Felspar	0.1-2.1
Biotite	1.4
Pyrite	100- 77,000
Marcasite	26-126,000
Chalcopyrite	10 - 5000
Fe(III)-oxyhydroxides	76,000

Table 4 Arsenic content (µ g/kg) in certain coal samples from NE India[3]

State	Sample	As range
Assam	Lignite	80-207
Assam	sub-bituminous coal	44-78
Nagaland	Lignite	56-68
Meghalaya	sub-bituminous coal	106-238
Arunalchal Pradesh	Graphitic shale	39-50

reducing conditions over a wide pH range of 6.5 to 8.5 that is typical of natural groundwater.

In natural waters arsenic is mostly found in inorganic form as oxianions of trivalent arsenite (As (III)) or pentavalent arsenate (As (V)). At the near-neutral pH, typical of most groundwater, the solubility of most trace-metal cations is severely limited by precipitation as, or co-precipitation with, an oxide, hydroxide, carbonate or phosphate mineral, or more likely by their strong adsorption to hydrous metal oxides, clay or organic matter. In contrast, most oxianions including arsenate tend to become less strongly sorbed as the pH increases<sup>[29]</sup>. Under some conditions these anions can persist in solution at relatively high concentrations (tens of  $\mu\text{g/L}$ ) even at near-neutral pH values. Relative to the other oxianion-forming elements, arsenic is among the most problematic in the environment because of its relative mobility over a wide range of redox conditions. Under oxidizing conditions,  $\text{H}_2\text{AsO}_4^-$  is dominant at pH less than about pH 6.9, while at higher pH,  $\text{HAsO}_4^{2-}$  becomes dominant.  $\text{H}_3\text{AsO}_4^0$  and  $\text{AsO}_4^{3-}$  occur under oxidizing and extremely acidic and alkaline conditions respectively. Uncharged  $\text{H}_3\text{AsO}_3^0$  occurs under reducing conditions at pH below 9.2<sup>[30]</sup>. In the presence of extremely high concentrations of reduced sulfur, dissolved arsenic-sulfide species may be significant. Reducing and acidic conditions favor precipitation of orpiment ( $\text{As}_2\text{S}_3$ ), realgar ( $\text{AsS}$ ) or other sulfide minerals containing co-precipitated arsenic. Therefore high arsenic waters are not expected where there is high concentration of free sulfide<sup>[31]</sup>. Thus in any study of this kind speciation data together with the degree of protonation is very important.

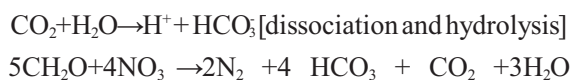
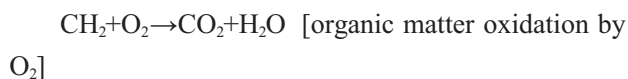
## 4 Mobilization of Arsenic in groundwater

The effect of pH and redox potential on the mobilization of arsenic has been studied extensively. The contribution of arsenic from sediments to overlying waters is substantial with decreasing pH value (Mok and Wai, 1990). At low pH, metal ions (Fe

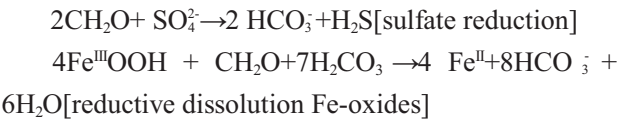
and Mn) are solubilized from the sediments with concurrent release of arsenic species. At high pH, increment in hydroxide concentration causes displacement of the arsenic species from their binding sites in a ligand exchange-type reaction. Under oxidizing conditions, As (V) is the major arsenic species in the sediments, where it co-precipitates with iron oxides and is held by iron oxides. Thus the solubility of arsenic under such conditions is very low. However, under reducing condition arsenic mobilization is controlled by the dissolution of hydrous iron oxides. Under oxidizing conditions the amount of arsenic released increases by 10 to 13 fold compared to aerobic conditions. Under aerobic conditions As (III) is the dominant species released into the aqueous system. This condition reduces ferric iron to ferrous iron releasing As (V), which in turn reduces to As (III)<sup>[32]</sup>.

Sediments are very good absorbers of As (V). Transformation from As (V) to As (III) takes place in these sediments depending on the prevailing Eh conditions. Relative to other arsenic species, As (III) is highly mobile in aqueous system. As (III) thus released from the sediments forms  $\text{AsO}_3^{3-}$  (Arsenite) and are strongly adsorbed onto clays, Fe and Mn oxides and hydroxides and organic matter.

Arsenic solubilization at low and high pH values as well as under reducing conditions is considerable<sup>[32]</sup>. On a regional scale, acid precipitation (including acid mine drainage) is probably an important factor affecting the mobility of arsenic and other metals in surface waters such as rivers. For example, lime water is commonly used to treat acid mine drainage. The resultant wastewater attains very high pH thereby aiding in release of arsenic from such sediments with which the wastewater comes into contact. The principal redox reactions aiding the release of arsenic are given below<sup>[9]</sup>:



[dentrification]



Besides the redox reactions shown above, organic carbon in soils play a significant role in mobilizing arsenic into the groundwater. West Bengal in particular and the entire Bengal basin in general is a loci for jute cultivation. Jute belongs to the plant family of Chorchorus. Jute is used for making carpets, bags, tarpaulins, ropes, strings and several other handicrafts. During its growth period the plant requires plenty of water. After harvesting, the plants are tied into bundles and allowed to “ret” (decompose) in ponds. In west Bengal groundwater from tube wells (with arsenic content  $>3 \times 10^{-6}$ ) is being used for this purpose. During the process of retting, a huge amount of organic carbon accumulates at the base of the pond and mixes with the soil. Recent field and experimental investigation on such soils indicates that the organic carbon rich matter plays an important role in fixing the mobilizing arsenic into the shallow aquifers<sup>[33]</sup>.

5 Bioaccumulation of As in food crops

It is well known that the soluble inorganic arsenicals are more toxic than the organic ones, and the trivalent forms (AsIII) are more toxic than the pentavalent ones (AsV). In fact inorganic arsenic compounds are classified as carcinogenic by the International Agency for Research in Cancer (IARC). Ingestion of large doses of arsenic usually results in symptoms within 30 to 60 minutes, but may be delayed when taken with food. Acute arsenic poisoning usually starts with a metallic or garlic-like taste, burning lips and dysphasia. Violent vomiting may ensue and may eventually lead to hematemesis. Continuous exposure to lower levels of arsenic results in adverse health effects that are being experienced by a large population in West Bengal and Bangladesh. Accumulation of arsenic in certain human parts like hair (180-20340  $\mu$  g/kg) and nails ( 380-44890  $\mu$  g/kg;

Mukherjee et al., 2006) is not commensurate with the arsenic contaminated water intake by a single person in a day. This has necessitated rethinking on arsenic pathways into human system. Recent work indicates that, besides groundwater, food crops constitute a major pathway of arsenic into human system <sup>[4,34]</sup>.

In West Bengal, groundwater used for irrigation contains 0.05 and 3.7 mg/L of arsenic <sup>[4]</sup> while it is higher in irrigation water ( 0.14- 0.55 mg/L; <sup>[34]</sup>). In the light of this, detailed investigation, in an area in West Bengal, has been carried out related to the distribution, speciation and mobility of arsenic in the soils of paddy and wheat fields and also on the concentration of arsenic in different parts of rice (Boro and Aman variety) and wheat plants taken from the same soils <sup>[4]</sup>. The groundwater used for irrigation in this area varies from 519 to 782  $\mu$  g/L. Boro is cultivated using groundwater from December to May while Aman is cultivated from July to December using rain water. Arsenic content in different parts of rice and wheat plants and in respective soils is given in table 5<sup>[4]</sup>.

Similarly, arsenic content in vegetables grown using groundwater with high arsenic content in West Bengal and Bangladesh has been reported by several workers <sup>[34,35]</sup>. Arsenic content in vegetables and cereals grown using groundwater with 85 to 108  $\mu$  g/L of arsenic content in several districts in West Bengal varies from 20-21  $\mu$  g/kg, 130-179  $\mu$  g/kg, respectively <sup>[3]</sup>. This concentration is 300% greater compared to the mean concentration generally reported in vegetables and cereals elsewhere in the world <sup>[36]</sup>. Due to repeated

Table 5 Arsenic content in the soils of rice and wheat and in different parts of rice and wheat plants

	As (mg/kg) in Rice	As (mg/kg) in wheat
Soil	7 to 10	10 to 17
Root	169-178	0.3-0.7
Stem	6 to 7	0.4-0.7
Husk	1	
grain	0.3	0.7

irrigation with such groundwater, soils, supporting the vegetables and cereals, also registered high arsenic content (10.7 mg/kg; [35]). It has also been reported that the arsenic uptake by plants is influenced by the amount of arsenic absorbed by soils and the plant species [34]. For example, “arum”, a leafy vegetable, which is widely consumed by the locals as a source of vitamin “A, C” and iron. Uptake of arsenic by this plant varies in the region. It is reported that in certain areas this plant has recorded arsenic as high as 138 mg/kg while in certain other areas the concentration is as low as 0.21 mg/kg [34]. Thus people consuming 100 mg of arum that contains 0.22 mg/kg of arsenic will meet maximum daily allowable limit of arsenic by eating only arum. According to provisional tolerable in take value of arsenic, an adult male can consume 9-11  $\mu$  g/kg body weight/day while an adult female can consume 11 -13  $\mu$  g/kg body weight/day of arsenic [22]. Children below 10 years can consume 12-15  $\mu$  g/kg body weight /day of arsenic. Thus consuming small quantity of arum with 138 mg/kg of arsenic will far exceed the limit set by WHO. This gives an idea of the amount of arsenic ingested by people daily through vegetables alone. Even food cooked with arsenic contaminated groundwater showed high values (0.12 -1.45 mg/kg; [34]) and fell well above the limit recommended by WHO. This clearly shows that bioaccumulation of arsenic (in food crops) is strongly influenced by the irrigated water, soil type, its chemical and physical characteristics, micro-organisms [3]. Accumulation of arsenic by food crops resulted due to irrigation practice adopted by the local population for prolonged periods.

## 6 Health effects

Arsenic has long been associated with toxic effects, producing marked impacts on health after both oral and inhalation exposures. Effects range from acute lethality to chronic effects, such as cancer and diseases of the vascular system. It is recognized that the soluble inorganic arsenicals are more toxic than the organic ones, and the trivalent forms (AsIII) are more toxic

than the pentavalent ones (AsV). In fact inorganic arsenic compounds are classified as carcinogenic by the International Agency for Research (IARC). In cancer arsenic toxicity, as evident from cases mentioned above, affects almost all the organs of the human body (e.g. Table 2). Ingestion of large doses of arsenic usually results in symptoms within 30 to 60 minutes, but may be delayed when taken with food. Acute arsenic poisoning usually starts with a metallic or garlic-like taste, burning lips and dysphasia. Violent vomiting may ensue and may eventually lead to hematemesis. Continuous exposure to lower levels of arsenic results in adverse health effects as described earlier.

### 6.1 World scenario

In countries like India, Bangladesh, China, Thailand, Vietnam, Taiwan, Hungary, Mexico and Finland, groundwater used for drinking contains elevated levels of arsenic [37-41]. Nearly 50 million people are at risk of cancer and other arsenic related diseases due to consumption of high arsenic groundwater in India and Bangladesh [9,42]. In several Latin American countries, like Argentina and Chile, high concentrations of arsenic ( $>10 \mu$  g/L) are reported in natural water [43-48]. In the Chaco-Pampean Plain (CPP; ca. 978,634 km<sup>2</sup>) of Argentina and in some local areas in the Andean ranges high arsenic (100-4800  $\mu$  g/L) and fluoride (0.1-6 mg/L) concentrations are found in groundwater. At least 1200 000 people, predominantly from rural CPP areas depend exclusively on arsenic contaminated groundwater resources. Arsenic and fluoride levels in these areas exceed the national drinking water limits of 50  $\mu$  g/L As and 1.7 mg/L respectively [47]. These limits are however higher than the WHO limits for As (10  $\mu$  g/L) and fluoride (1.5 mg/L) [22].

### 6.2 West Bengal scenario

In West Bengal, as mentioned above, 44 % of the total population of 88 million (2001 census) are suffering from arsenic related diseases. About 72 % of them live in rural areas and are agrarians by profession. Nearly 7 % of the people affected by arsenic



poisoning are children. The severity of the situation can be seen from the pictures shown in figure 2.

Previous investigations considered that only the shallow aquifers were contaminated with arsenic in West Bengal [8]. Subsequent investigations have clearly demonstrated that even the deep aquifers in several regions of the district are contaminated with high content of arsenic [8,20]. The arsenic content in groundwater in the West Bengal aquifers vary from 0.05 to 3.7 mg/L, with an average of 0.2 mg/L. The Bengal Basin stratigraphy shows that the basin has 3.5 km thick sedimentary sequence over the Rajmahal Traps. The sedimentary sequence varies in age from Recent to Paleocene (Figure 3 [7]) .

The entire sedimentary sequence acts as an aquifer and is composed of sub-rounded to sub-angular, fine to

medium grained sands with occasional intercalations of clay lenses [8]. This aquifer is divided into sub-aquifers, on a local scale, by clay lenses. On a regional scale it is difficult to classify the entire aquifer system into shallow, intermediate and deeper aquifers as has been reported [8].

7 Arsenic removal techniques

Over the past two decades, several research laboratories across the world have developed arsenic removal techniques from groundwater to provide safe drinking water to the rural population.

Oxidation, coagulation and ion exchange process are some of the methods commonly adopted to remove arsenic from drinking water. In oxidation technique, As (III) is oxidized to As (V) by using oxidants like

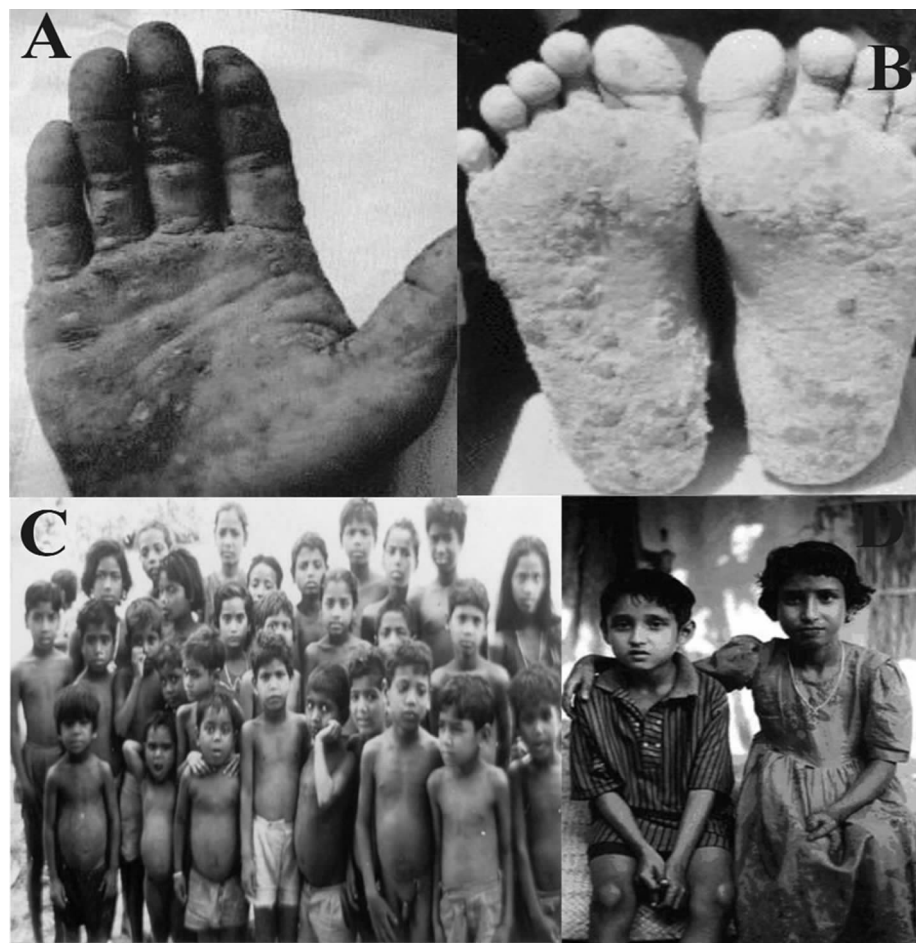


Fig.2 Pictures showing the effect of arsenic poisoning in West Bengal

A-Arsenic affected hand; B-Arsenic affected feet; C-A group of children affected by Arsenic poisoning; D-Growth disorder in children due to arsenic poisoning



(-200mV) the soluble arsenic content increases by 13 folds as compared to 500 mV<sup>[58]</sup>. Maximum conversion of As (V) to As (III) takes place under redox potential of + 100 mV and below. Around +150 mV besides iron manganese also gets mobilized into the aqueous phase releasing arsenic into the solution. This process has been recognized in the field conditions also around Murshidabad, where dissolution of both iron and manganese oxides are responsible for increasing the arsenic levels in groundwater (Stueben et al., 2003). The most interesting experimental finding relevant to the conditions prevailing in West Bengal is that reported by Onken and Hossner<sup>[59]</sup>. According to this experiment, soil solution under flooding conditions recorded maximum concentration of arsenic compared to the soils under non-flooding conditions. Release of soluble arsenic under flooding conditions takes place in a few hours of flooding.

Thus there seems to be an analogy between experimental work and flooding of rice fields in West Bengal. Recent work on arsenic content in rice and wheat plants from West Bengal indicates very high arsenic content in rice roots ( $169 \times 10^{-6}$ - $179 \times 10^{-6}$ ;<sup>[423]</sup>) while the wheat roots have relatively low arsenic content ( $0.3 \times 10^{-6}$ - $0.7 \times 10^{-6}$ ; Norra et al., 2005). The arsenic content in leaves, husk and the rice grain is  $7 \times 10^{-6}$ ,  $1 \times 10^{-6}$  and  $0.3 \times 10^{-6}$  respectively. It is not clear whether this arsenic locked in the food grains has entered the food chain or not. Similar problem of arsenic contaminated rice is reported from Bangladesh<sup>[24]</sup>.

The present rice cultivation practice in India is to plough the roots of the rice plants back into the soil after harvesting. Due to change in redox conditions during the subsequent crops, the arsenic in rice roots gets mobilized and infiltrates into the shallow aquifers. Thus arsenic flow cycle has been established in West Bengal due to tube well irrigation. In large parts of West Bengal both deep and shallow aquifers are contaminated with high levels of arsenic. Thus the roots of the rice plants are accumulating high levels of arsenic drawn from arsenic rich deep aquifer

groundwater and systematically supplying it to the shallow aquifers<sup>[5]</sup>.

## 9 Isotopic signatures in groundwater

World over  $\delta^{18}\text{O}$ ,  $\delta\text{D}$  (origin and evolution),  $^{14}\text{C}$ ,  $^{13}\text{C}$  (organic pollution and paleowater dynamics),  $^{34}\text{S}$  (pollution source),  $^{15}\text{N}$  (nitrate source),  $^{11}\text{B}/^{37}\text{Cl}$  (salinity source and water rock interaction) isotopes are widely used for various uses mentioned. However, arsenic isotopic investigation has not been carried out so far for groundwater of West Bengal. Out of all arsenic isotopes  $^{73}\text{As}$  has fairly large half life of 80 days<sup>[60]</sup> and appears to be very useful in identifying the source (s) of arsenic in groundwater of West Bengal. Investigation on  $^{73}\text{As}$  concentration in fly ash from the thermal plants, aerosols over West Bengal, pyrite minerals in the aquifer sediments and coal beds would definitely help in understanding the various sources contributing arsenic to the groundwater system in the Bengal basin. Perhaps the best way to initiate this work is to collect the first rain water over Bengal basin and analyze arsenic isotope signatures.

## 10 Conclusions

Thus, though arsenic pollution in the groundwater in West Bengal is geogenic, recycling of arsenic is due to the prevailing irrigation practices mixed with the entire aquifer systems and the contamination of all the aquifers. The present existing arsenic removal techniques mentioned above cannot be implemented in rural areas, due to the prevailing socio-economic status of the population. Now that arsenic has entered the food chain due to irrigation practices, immediate solution to partially solve this problem is to use surface water for irrigation. The arsenic content in surface water in the rivers of West Bengal is about  $1.9 \mu\text{g/L}$ <sup>[9]</sup>. Evolving a network of canals from the existing river system is the most economically and acceptable solution to reduce incidence of arsenic related diseases in the rural West Bengal. Though it has been established that arsenic is geogenic, the exact source(s) contributing large quantities of this element to the



groundwater system is poorly understood. Perhaps arsenic isotopic investigation may solve this problem in future.

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## 西孟加拉地区地下水砷污染

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**摘要:**目前,西孟加拉地区地下水砷污染问题日益严重并且已经波及到食物链中。由于吸收了砷污染地下水,谷物和蔬菜中砷含量日渐累积,超出了健康规定范围。尽管提出了若干补救方案,但是考虑到农业人口的社会经济状况,建议使用地表水灌溉方案。然而,实际中该方案仍然较难施行,且并无其他更经济有效的措施。若干年后,含水层可以减缓严酷的健康环境现状并为人们提供安全的饮用水。

**关键词:**砷污染;西孟加拉;砷的生物积累;砷与管井

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