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ARSENIC POLLUTION IN GROUND WATER - A STATUS REPORT



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ABSTRACT

Increasing threat of pollution of surface water bodies due to the continuous and unabated discharge of wastewater originating from municipal, industries, and agricultural sectors is posing more pressure to the available ground water sources.

Over exploitation of ground water sources for various designated uses, such as; drinking, domestic, industrial, and agricultural sectors are eventually inviting threat to the ground water sources both in terms of quantity and quality. Hazards of increasing public health related problems have made or are making people more aware about the quality of water irrespective of whatever quantity is assured. The need of the time is thus supply of right quality of water at the right time.

Waters - surface and under ground- usually get contaminated by the organic and inorganic substances and its threat towards pollution depends on the degree of concentration of polluting substances. There are many reasons of pollution of waters, however, most of the causes, if not all, are due to the consequences of man-made activities.

Arsenic pollution in ground water is not a new problem. Many Countries in the World had experienced menace of arsenic pollution in water and sacrificed many lives. Causes of arsenic pollution were different in different countries. However, the main source of arsenic occurrence in water had been thought to be due to the degradation of natural environment.

The arsenic pollution in ground water in West Bengal has been described as the World biggest calamity. Eight districts within the Bhagirathi-Hoogly river basins covering an area of 37,493 km² with more than 4.5 million people are affected by the arsenic pollution. The source of occurrence of arsenic has been reported to be of geological formation of source material. Occurrence of iron-pyrite and the change of geo-chemical environment due to over-exploitation of ground water or excessive fluctuation of ground water table have been thought to be the reason of decomposition of pyrites to ferrous sulphate, ferric sulphate and sulfuric acid. However, no definite explanation regarding the source of arsenic could be given. The concentration of arsenic is mostly dominant in the intermediate layer and are being spreaded over the time and space in the linear track starting from Malda district towards South 24-paraganas district. The interesting feature of arsenic pollution is that it has a positive co-relation with the iron concentration.

A number of research organizations and departments are involved in monitoring the menace of arsenic pollution in ground water in West Bengal. Different agencies have taken this problem as a challenge and on the way to develop appropriate technologies for removal of arsenic from water.

However, unless reasons and sources of arsenic pollution are found out, and thereby an appropriate scientific management with a view to protect the spreading of arsenic pollution is thought, it would be difficult to combat the problem and the risk as well. A proper water-shed management and conjunctive use of surface and ground water may perhaps be an approach.

The report addresses compilation of information about arsenic pollution in ground water experienced by many countries in the world and problems in eight districts West Bengal in particular. The science of arsenic pollution and the state-of-art of arsenic removal have been discussed. Some immediate remedial measures have also been suggested.

1.0 INTRODUCTION

Water is an integral part of our life and has been well recognized as nectar. Therefore, conservation and management of water both of its quantity and quality, on sound lines are necessary for the general well-being of all life. For maintaining good living standards we need ample water resources, particularly because we, in India, use considerable amount of water.

Water is used for a number of uses, such as; i) Irrigation and Livestock, ii) Power, iii) Industry, and iv) Domestic. India receives 3 trillion m^3 of water per year through rain in which quantity of water available for use is 1900 $M m^3$ per year. It has been estimated that out of the 1900 $M m^3$ of water available/year in India (Khoshoo, 1986), the projected use pattern by 2000 AD will be 1092 $M m^3$, in which 869 $M m^3$ in Irrigation and Livestock, 150 $M m^3$ in Power, 35 $M m^3$ in Industry, and 38 $M m^3$ in Domestic sector. The estimated total ground water available is 210 billion m^3 . These figures certainly reflect that quantity of water available is much more higher than the projected demand. There is also an illusion that water is abundant and unlimited. This is because we never pay for the true cost of water that we use in field, industry and at home. In one sense, it is true that water is abundant but the total water available in various forms can not be used for different uses.

Increasing threat of pollution due to the man-made activities and natural phenomena, threat towards the quality of available fresh water is also rising in a faster rate. In some areas, the stage of water pollution due to organic and in-organic substances, is such that scarcity of water even for drinking is reported to be acute. The shortage of water in Tamil Nadu, a few years back, is indeed the shape of things to come. This was a warning to our planners and decision makers to start thinking very seriously about water conservation, and management in agricultural, industrial and urban sectors. Since, use of water and its return after use in the form of wastewater, is a continuous processes and the demand of water for various uses are in the rise due to the increase in population and their allied activities, time delay in conservation and management aspects may invite a number of environmental and social hazards originating

from water. Some of the recent continuing incidents with origin from water witnesses our ignorance in the conservation and management of water. To mention few important one, arsenic pollution in groundwater in West Bengal, and increase in fluoride concentration in groundwater, have been reported in many places besides the pollution threat to the surface water, particularly in rivers.

Amongst various uses of water, its use for drinking purpose is the most important one. Both surface and groundwater are used as drinking water sources. Pollution of surface water in developing countries like ours are increasing day by day, hence, its use for domestic purpose is becoming scarce and getting dis-appreciated amongst the users. Groundwater has, therefore, become the most important source for drinking water. Besides drinking water, groundwater is also used for irrigation and industrial uses. Re-used water, directly or in-directly get their pathways to the groundwater also. Although it seems that groundwater is more protected than surface water against pollution, it is still subject of pollution, whether is man or natural. Moreover, once pollution of ground water occurs, its restoration to the original, non polluted state is more difficult. Therefore, the threat of ground water quality is also a serious concern. The adverse effects on groundwater quality are the result of man's activity at ground surface and also due to the natural phenomena. Further, the quality of groundwater is governed by the composition of dissolved solids in it and also due to the geological formation in which it is preserved.

Because of multi-facet uses of groundwater, following common questions always arise:

From general perspectives

- i. Whether quality of groundwater, in whatever form it is available, is suitable for drinking ?
- ii. Whether or not, the use of fertilizers & pesticides on agricultural land affects the quality of percolated water that feed the ground water storage ?
- iii. Whether over exploitation of groundwater without regarding the geohydrology of the area is advisable ?
- iv. Whether surface disposal of both solid and liquid wastes in unscientific manner is appropriate ?

From research point of view

- i. What are the sources of problematic solutes and the processes controlling their concentrations and behaviours in the aquifers ?
- ii. Will concentration increase or remain stable due to abstraction of groundwater ?
- iii. What are the remedial measures or treatment ?
- iv. What happens when air enters the saturated zone due to drawdown of piezometric levels in the aquifer ?

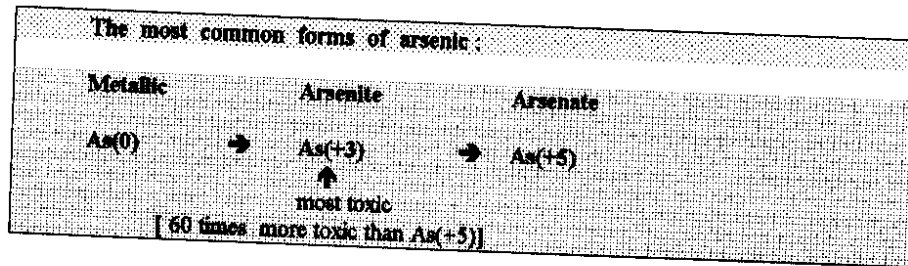
In recent years, pollution of aquifers, in general, have become an important issue to the groundwater managers. For example, arsenic pollution in ground water in some districts of West Bengal is a grave concern in the national and international perspectives. The problem of arsenic pollution in groundwater in West Bengal has been reported as World's biggest episode of arsenic pollution. Beside this, contamination of groundwater from the leaching of wastes have also been reported in many places. Conservation of groundwater sources and management of groundwater quality have become the need of the time.

In this report, it has been attempted to compile information about arsenic pollution and give a state-of-art of arsenic pollution. The problem of arsenic pollution in groundwater in West Bengal has also been discussed and critically analysed .

2.0 ARSENIC ?

Arsenic (As), an element belonging to the fifth group in the periodic chart of the elements, is classified as a metalloid. It is an element possessing both metallic and non-metallic properties. It exists in three distinct form; viz., metallic [As(0)], trivalent arsenite [As(+3)], and pentavalent arsenate [As(+5)]. Compounds containing arsenic can be organic as well as inorganic. Main arsenic species are inorganic arsenite, arsenate and organic dimethylarsinic and monomethylarsonic acids and the distribution of arsenic between these forms is dynamic . Arsenic has a high affinity for sulfur and sulfur-containing compounds such as thiols. The trivalent inorganic species are most toxic forms of arsenic, though the other

forms are also toxic to some degree in mammals as well as to aquatic life. Arsenite has been reported to be 60 times more toxic to human beings than the arsenate ions. From greatest to least, arsenic toxicity is as follows: arsine (valance -3), organo-arsine compounds, arsenites (+3) and oxides (+3), arsenates (+5), arsonium metals (+1), and native arsenic(0). Dissolved arsenic in natural water is usually found primarily as arsenite or arsenate.



Although there exists a number of opinions whether arsenic is a carcinogen , and the minimal levels of exposure necessary for the onset of various symptoms, studies clearly demonstrated that arsenic concentrations adversely affect human health and the environment (Welch et al., 1988) . In fact, the geochemical processes is responsible for elevated arsenic concentrations in different hydrologic settings. The geochemistry of arsenic is complex and is affected by a variety of processes, including mineral dissolution-precipitation, oxidation-reduction, and adsorption, as well as biologically mediated reactions. An understanding of these processes is needed for effective water resources management.

3.0 SOURCES OF ARSENIC

Following are the sources of arsenic :

Environment

- Rainwater and snow,
- Rivers & Laks,
- Sea water.

4.0 CHARACTERISTICS OF ARSENIC IN THE ENVIRONMENT

Arsenic is widely distributed in the environment, and as consequence of increased concern about environmental pollution, there is a growing demand for knowledge about arsenic content in soils, water, air, foods, and beverages. Forms of naturally occurring arsenic observed in the natural environment have been described in Figure-1 .

Studies on the bio-chemical cycles of arsenic show that there are different oxidation states of arsenic. Its toxicity, biological properties, bio-availability and geochemical activity depend on the chemical form of arsenic. Therefore, it is of interest to know not only the total arsenic content, but the speciation of the arsenic.

Dissolved arsenic concentrations in natural waters (excluding ground water) are listed in Table-1. Arsenic concentrations in rain derived from unpolluted oceanic air masses averages 0.46 µg/l, and from rain through terrestrial air masses also averages to 0.46 µg/l.

Table -1 : Arsenic Concentration in Water Other Than Ground Water

Source	Arsenic (µg/l)
Rainwater and snow ¹	< 0.002 -0.59
Rivers ²	0.20 - 264
Lakes ²	0.38 - 1,000
Sea water ³	0.15 - 6.0

(Sources : 1- Andreae, 1980, 2 - Benson and Spencer, 1983, 3 - Kanamori, 1965; Onishi and Sandell, 1955)

Higher than the average arsenic levels in precipitation are often associated with anthropogenic sources, such as emissions from smelters which resulted in abnormally high arsenic concentrations in surface sediments. Thus, the source of arsenic in the sediments has the origin either from rain water or from other natural reasons. It is unusual to find high arsenic concentrations in river water without a significant contribution of arsenic from geothermal water or mineralized areas.

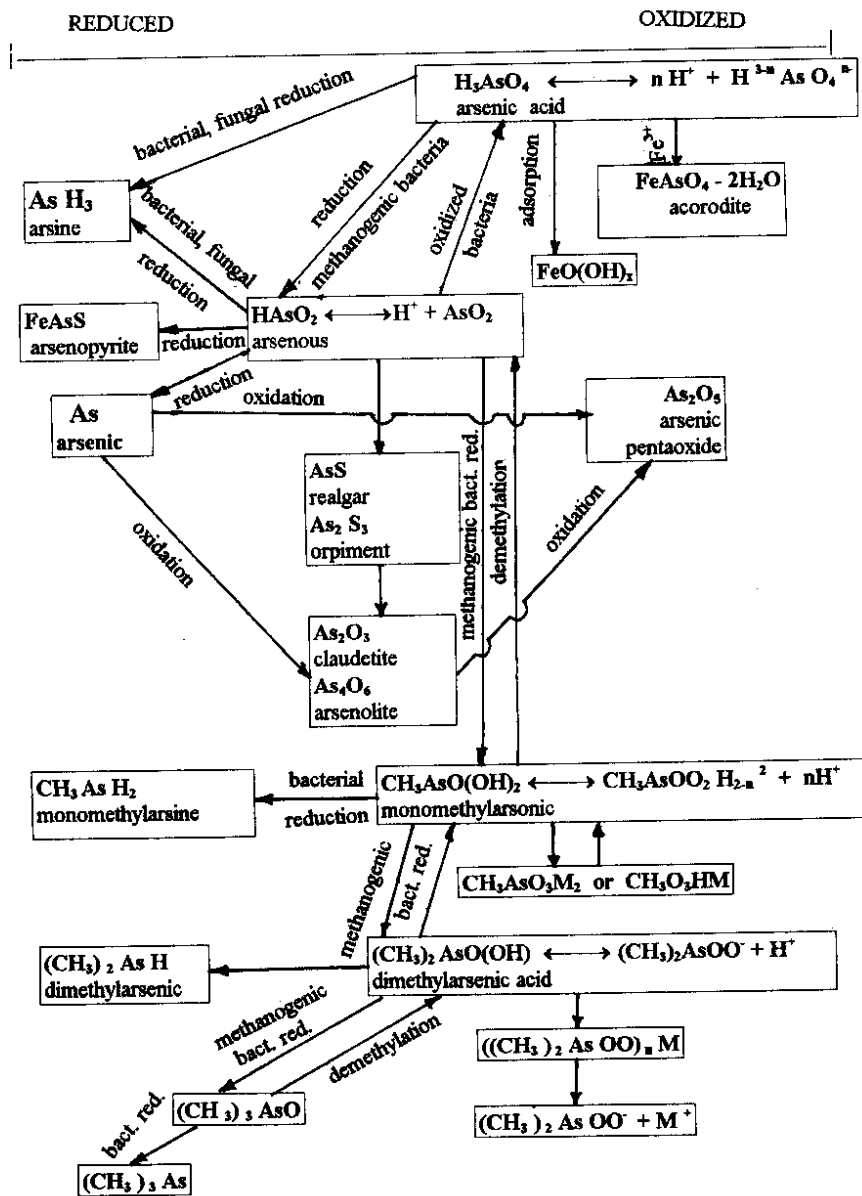


FIGURE - 1: FORMS OF NATURALLY OCCURRING ARSENIC FOUND IN THE NATURAL ENVIRONMENT (after Braman, 1975).

Arsenic concentrations in igneous, metamorphic, and sedimentary rocks generally are the major source of aqueous arsenic. Tables - 2 & 3 summarize arsenic concentrations in rocks and sediments.

Table - 2 : Arsenic Concentrations in Rocks

Type of rock	Arsenic (mg/l)
<u>1.0 IGNEOUS¹</u>	
<u>Ultrabasic :</u>	
Peridotite, dunite, serpentinite	0.3 - 15.8
<u>Basic :</u>	
Basalt (extrusive)	0.18 - 113
Gabbro (intrusive)	0.06 - 28
<u>Intermediate :</u>	
Latite, andesite, trachyte (extrusive)	0.5 - 5.8
Diorite, granodiorite, syenite (intrusive)	0.09 - 13.4
<u>Acidic :</u>	
Rhyolite (extrusive)	3.2 - 5.4
Granite (intrusive)	0.18 - 15
<u>2.0 METAMORPHIC ROCKS¹</u>	
Quartzite	2.2 - 7.60
Slate/phyllite	0.50 - 143
Schist/gneiss	0.00 - 18.50
<u>3.0 SEDIMENTARY ROCKS^{2,3,4}</u>	
<u>Marine :</u>	
Shale/claystone (nearshore)	4.0 - 25.0
Shale/claystone (offshore)	3.0 - 490.0
Carbonates	0.1 - 20.0
Phosphorites	0.4 - 188
Sandstone	0.6 - 9.0
<u>Nonmarine</u>	
Shales	3.0 - 12.0
Claystone	3.0 - 10.0

(Sources : 1 - Boyle and Jonasson, 1973, 2 - Tourtelot, 1964, 3 - Gulbrandsen, 1966, 4 - Onishi, 1978).

Table - 3 : Arsenic Concentrations in Sediments

Source	Arsenic (mg/l)
Marine :	
Muds ¹	3.2 - 10.0
Clays ¹	4.0 - 25.4
Carbonate ²	< 1.0
Stream/river ³	5.0 - 40.0
Lake ⁴	2.0 - 3.0
Soils ⁵	< 0.1

(Source : 1 - Onishi, 1978, 2 - Turekian and Wedepohl, 1961, 3 - Wilson and Hawkins, 1978, 4 - Benson and Spencer, 1983, 5 - Boermgen and Shacklette, 1981).

Difference in arsenic concentration does not exist among the various types of igneous rocks. Arsenic does, however, concentrate in some minerals. For instance, arsenic readily substitutes for silicon, ferric iron, and aluminum in crystal lattices of silicate minerals (Onishi and sandell, 1955). As a result, arsenic concentration tend to be relatively high in volcanic glass, aluminosilicate minerals, and igneous rocks containing iron oxide. Because the arsenic content of metamorphic rocks is dependent primarily on source-rock composition, arsenic concentrations are highly variable within this rock type. Sedimentary rocks generally contain higher arsenic concentrations than igneous and metamorphic rocks. Tourtelot (1964) found that, in general, arsenic in nonmarine shales/clays is absorbed by clay minerals, whereas the arsenic associated with marine shales/clays is present in pyrite and organic matter. Sandstones and carbonate rocks are comparatively low in arsenic, averaging only 1 milligram per kilogram. High arsenic concentrations in phosphorites were observed positively correlated with the organic (Gulbrandsen, 1966) and iron content (stow, 1969) of the rock. Comparisons of the data (Tables 1 & 3) indicate that suspended and bottom sediments in most aquatic systems contain much higher arsenic concentrations than those of the water. The capacity of sediment to retain and concentrate arsenic is controlled primarily by grain size (Horowitz, 1984),

because smaller grain sizes have a greater surface area and a greater adsorption capacity per unit weight. Clay minerals, organic matter, iron, and manganese oxides, which commonly occur as coatings on sediments, commonly adsorb trace elements such as arsenic. In soils, organic matter can concentrate arsenic in the upper horizons while adsorption onto ferric oxyhydroxide can enrich arsenic at greater depth. Arsenic in certain solid phases within sediments particularly iron oxides, and organic matter may be the primary source of arsenic in ground water.

Arsenic can exist in many oxidation states in the natural environment including +5, +3, +1, and -3 valences, and rarely in elemental (neutral) form. In these different oxidation states, arsenic can form many inorganic and organic compounds. The toxicity of arsenic compounds depends largely on the oxidation state.

5.0 PROCESSES CONTROLLING ARSENIC DISTRIBUTION IN GROUND WATER

Arsenic in ground water is generally present as an oxyanion, as arsenate ($H_2AsO_4^{3-}$) or arsenite ($H_2AsO_3^{3-}$), or both. The dominant aqueous species, under varying pH and redox conditions at equilibrium are shown in Figure - 2. The distribution between arsenite and arsenate is not, in all cases, predictable from other measurements of Eh. The Eh values calculated using analytical data do not agree well with either each other or the value measured in the field. The ratio of arsenite to arsenate in that case cannot be estimated using analytical data for other redox couples or field Eh measurement in the ground water system. Using the standard diagram as represented in fig. 2 can be used for obtaining the distribution of arsenite and arsenate in the water at known Eh and pH values.

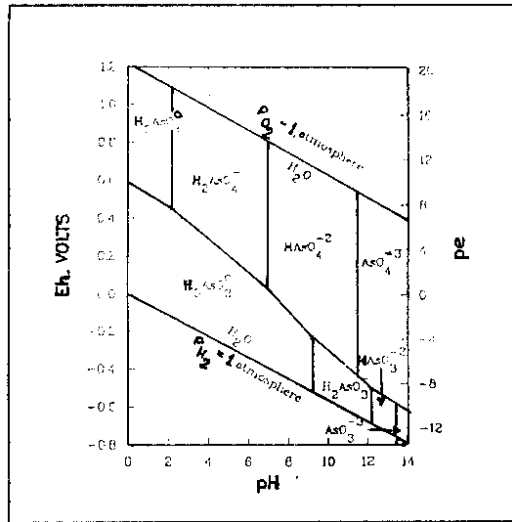


FIGURE - 2 : Fields of stability for dissolved forms of arsenic as a function of Eh and pH at 25 degree Celsius.

Major processes responsible for observed concentrations of arsenic in ground water include mineral precipitation/dissolution, adsorption/desorption, chemical transformations, ion exchange, and biologic activity. Factors such as pH, Eh, solution composition, competing and complexing ions, aquifer mineralogy, reaction kinetics and hydraulics of a ground-water system can all potentially affect the arsenic concentrations.

Thermodynamic calculations, along with mineralogical identification, are major tools used by geochemists to evaluate whether mineral precipitation and dissolution reactions control concentrations. Mineral precipitation can limit aqueous arsenic concentration in ground water. The commonly identified arsenic-bearing minerals are regular (AsS), Orpiment (As_2S_3), arsenopyrite ($FeAsS$), Claudetite (As_2O_3), arsenolite (As_4O_6), arsenic pentoxide (As_2O_5), and scorodite ($FeAsO_4 \cdot 2H_2O$). Within this group of minerals, arsenopyrite is the most common arsenic mineral (Welch, et al, 1987). Alkaline-earth and transition-metal arsenates also may control the arsenic concentrations in groundwater. Barium arsenate has been found to be a possible control on arsenic concentrations on the basis of its low solubility (Wagemann, 1978).

Arsenic can also substitute to varying degrees for other elements in minerals such as pyrite, which is commonly found in both fossil and active geothermal systems, and iron oxides formed at low temperatures. Arsenic from aluminosilicate mineral had not been found to be responsible for elevated arsenic concentrations.

In general, geothermal water has higher arsenic concentrations than nonthermal water. The geo-chemical controls and sources of arsenic in geothermal systems are not well understood, although, the relation between chloride and arsenic at Yellowstone and Lassen have been found to lead the interpretation and the aqueous arsenic may be derived largely from leaching of the aquifer matrix. No evidences are available representing high concentration of chloride coincides with high arsenic concentrations in geothermal water. Arsenic concentrations greater than 1000 $\mu\text{g/l}$ generally have chloride concentrations of average 800 mg/l or greater. The lack of general positive correlation between arsenic and chloride conc. had been observed to be due to the result of different controls and sources of concentrations of chloride in geothermal water, including evaporation of conc., dissolution of halite in some sedimentary environments, or differing arsenic to chloride ratios in various rocks types that have geothermal systems. The sulfide minerals orpiment (As_2S_3) and realgar (AsS), which commonly occur together, may control arsenic concentration. in some systems as evidenced by their presence in fossil in geothermal areas.

In nonthermal water unaffected by man's activities, elevated concentrations are most commonly associated with volcanically derived sediments. Adsorption (particularly in alluvial aquifers) and mineral precipitation-dissolution probably are the major geo-chemical controls.

Factors that limit the ability to define geo-chemical reactions responsible for arsenic concentrations in groundwater include:

- i. Thermodynamic data for the aqueous complexes and minerals of arsenic have not been critically evaluated,
- ii. Adsorption of trace constituents can be affected by a variety of factors, including competition with other anionic solutes for adsorption. Adsorption reactions are irreversible.

Adsorption and coprecipitation are also major factors controlling aqueous arsenic concentrations. Phases that may coprecipitate with or adsorb arsenic include hydrous oxides and hydroxides of iron, aluminum, manganese, and organic matter. It was observed from arsenic adsorption study on ferric oxyhydroxide that higher pH solutions have a lower adsorption capacity relative to more acidic solutions. The lower adsorption at higher pH values is related to the formation of a negative surface charge on ferric oxyhydroxide, resulting to an electrostatic repulsion between the sorbent and the arsenic anion.

Adsorption and coprecipitation of arsenic are affected by the presence of other solutes that can compete for adsorption. For instance, phosphate competes with arsenic for adsorption sites on iron oxide and soils.

Adsorption and coprecipitation of arsenic may not be fully reversible processes. The adsorption of arsenic species may be irreversible because the arsenite and arsenate are oxyanions similar to phosphate and selenite.

6.0 QUALITY CRITERIA OF ARSENIC POLLUTION

Water is used for various purposes. The criteria of water quality for various designated uses are different for different natural temperate region. The permissible limit of arsenic for different uses has also been specified in many countries, like other water quality parameters.

US-EPA's (Environmental Protection Agency) human health guidelines assume that carcinogenicity is a "non-threshold phenomena", that is, there are no "safe" or "no-effect level". The carcinogens are thus described as pollutant concentrations corresponding to increase in the risk of developing cancer.

EPA had specified water quality criteria for arsenic for two basic purposes: protection of aquatic life, and human health. Aquatic life criterion was described as "an estimate of the highest concentration of the substance in water which does not present a significant to the aquatic organisms in the water and "their uses" [the term "their uses" refers to consumption by

humans and wildlife]. However, for human health, it was described as the criteria which minimize or specify the potential risk of adverse human effects due to the substance in ambient water. The criteria for human health derived by US-EPA were based on two types of biological endpoints; i) Carcinogenicity and, ii) systematic toxicity. The criteria for "Arsenic Pollution" in water for various designated uses are tabulated below:

Table - 4 : US-Environmental Protection Agency's Criteria for Arsenic Pollution in Water

Fresh water	Sea water		Human Health (10 ⁻⁶ risk for carcinogens)		
	Chronic	Acute	Chronic	For consumptions of Water Organisms Organism only,	
µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
360	190	69	36	2.2	17.5

Source : US-EPS 40 CFR Part 131 (1992)

In India, uses of water have been designated for five different purposes, i) A- Drinking water source without conventional treatment but after disinfection, ii) B - Out door bathing, swimming, and recreation (organized), iii) C - Drinking water with conventional treatment, iv) D - Propagation of wild life fisheries, and v) E - Irrigation, industrial, cooling and controlled waste disposal. Among the various designated uses, water quality criteria for "Arsenic" is concerned for first three uses, and the tolerance limits have been prescribed by the Indian Standard Institutions (1982).

Table - 5 : Indian Standard for Arsenic Pollution

TOLERANCE LIMITS OF ARSENIC PRESCRIBED BY THE INDIAN STANDARDS INSTITUTIONS (1982)			
	A (mg/l)	B (mg/l)	C (mg/l)
	0.05	0.20	0.20
A :	Drinking water source without conventional treatment but after disinfection,		
B :	Out door bathing (organized),		
C :	Drinking water with conventional treatment.		
Source : Indian Standard (IS : 229 -1982)			
Tolerance limit of Arsenic (As) prescribed by U.S.-EPA(1975), World Health Organization (WHO), European Standards (1970), for drinking water			: 0.05 mg/l

7.0 CAUSES OF ARSENIC POLLUTION

Sources of arsenic in the natural environment and its use in the various sectors have been described in section-3. In this section, some of the known causes of arsenic pollution in surface and ground water are highlighted :

- i. Industries producing herbicides, paint pigments, copper and lead alloys, glass and electrical semi-conductor, produce arsenic as by-product which after mixing with surface water or percolating to the ground cause arsenic pollution,
- ii. Occurrence of arseniferous formation in the soil strata. Arsenious layers, if exist in soil layers, get oxidised when water percolate through the oxidation zone that helps oxidation of the arsenic to HAsO_4^{-2} anion,
- iii. Occurrence of Iron-pyrite in the litholog of ground water reservoir and the change of geo-chemical environment due to over-exploitation of ground water or excessive fluctuation of groundwater table can lead to the decomposition of pyrites to ferrous sulphate, ferric sulphate and sulphuric acid,
- iv. Geological formations of the source materials,
- v. Change of lithology can be a reason of occurrence of arsenic in ground water,
- vi. Use of heavy duty pumps for irrigation in the arsenious zone help to mix the waters in the isolated arsenious pockets in the aquifer leading to progressively wide incidence of arsenic contamination within recent years.

8.0 ARSENIC DETERMINATION TECHNIQUES

A variety of methods are available for determination of total arsenic, such as:

- i. Atomic Absorption Spectrometry (AAS) or Emmission Spectrometry (ES),
- ii. Microwave Emission (EM),
- iii. DC Helium method,
- iv. Differential Pulse Polarography (DPP),
- v. Hydride Generation technique (HG).

Amongst the above techniques, the most sensitive methods claimed to be Hydride Generation (HG) whereas, DPP technique though has been well appreciated but has been found to be laborious.

Usually for arsenic determination, arsine is first generated and then determined by AAS. However, it has reported that the detection limits by AAS is approximately 1 ng. arsenic, and it is difficult to measure small quantities of H_3As_4 by AAS. Moreover, by AAS it is not possible to measure differential oxidation states of arsenic.

The advantage with hydride generation technique is of distinguishing between arsenite, total inorganic arsenic, and methylarsenic compounds. Arsenite is selectively reduced by sodium borohydride to arsine in buffered media in the pH range 5.0 to 6.5. Arsenate and methylarsenic compounds require a pH of 1 for their reduction. The pH-controlled reduction of arsenite is one of the most frequently used methods for determination of arsenic compound. When arsenate and methylarsenic compounds are present in a solution in which arsenite is to be determined, the hydride generation method may not give reliable results.

The hydride generation method for determination of arsenite requires that arsenic compounds in the sample do not interconvert during the period between collection and analysis of the sample.

Polarographic Determination

Determination of As (+3) by DPP

Procedure : 10 ml of the sample at pH=0 is to be adjusted with hydrochloric acid and is to be pipetted into cell and then 10 ml of supporting electrolyte HCl 1 M and 2 g of the resin are to be added. Nitrogen is to be bubbled through the solution to remove the oxygen from the solution. The polarographic determination by DPP technique is to be carried out under the operational conditions.

The standard addition method is to be used for quantitative determination using Eppendorf pipettes and standard arsenic solutions (20, 50 and 100 mg/l). Nitrogen is to be bubbled through the solution for 10 min., and the polarograms are to be recorded.

Both sample and each aliquot are to be measured three times; the mean value is to be recorded in calculation. The amount of arsenic added is to be plotted versus peak current and the arsenic concentration is to be obtained from this curve. A linear response is to be obtained for the range of concentration between 20 and 170 mg/l.

Determination of Total Arsenic

Procedure : 5 ml of NaHSO_3 1 M is to be added to 5 ml of the sample at pH = 3 and the value is to be readjusted to pH = 3, with HCl 1 M. The solution is then to be transferred to a round bottom flask fitted with two openings. An air-condenser is to be connected to one of these openings and an inert gas, nitrogen, is to be bubbled through the second.

The solution is to be boiled for 30 minutes, is then to be allowed to cool and an excess of HCl or HClO_4 is to be added in order to eliminate the excess of HSO_3 as SO_2 by simultaneously heating and bubbling of nitrogen. The flask content is then to be completed to 10 ml with deionized water and the pH is to be adjusted to pH = 0.

Then the procedure described in As (+3) is to be followed.

Determination of As (+5)

The As(+5) content is to be evaluated by difference between total arsenic and AS(+3).

9.0 STATUS OF ARSENIC MENACE

9.1 Global Scenario

Occurrence of arsenic in ground water has been reported in many parts of the World. In United States of America, Alaska, Arizona, California, Oregon, Hawaii, Nevada and Washington faced the set back of arsenic concentration in ground water in 1987. The arsenic

concentration in the water supply of the Fallon, Nev Naval Air Station (NAS) was measured at 0.080 - 0.116 mg/l which exceeded the maximum contaminant level of 0.05 mg/l.

Incidence of arsenic poisoning in Terreon, Mexico (1963) where 496 people were used well water containing 4 to 6 mg/l of arsenic causing severe signs of poisoning in 15% of affected people.

In Autofagasta, Chilli, a large number of children were affected from arsenic contamination (0.80 ppm) in ground water in 1960 through leaching of arsenical wastes from mining operations into spring water. It was reported that majority of the children with chronic arsenic poisoning were from a low-socio-economic environment, and the reason of low nutritional states which favoured the toxic effects of arsenic, could not be ignored.

Arsenic contamination of streams and wells had been reported from OBUSI goldmine area of Ghana. From Trans-Baikalia province of Russia and also from Newwoaland arsenic contamination of ground water had been reported.

In Taiwan, high concentration of arsenic (0.53 - 1.19 ppm) in ground water was reported in 1967 and a sizeable population were affected from arsenic dermatosis. High concentration of arsenic in artesian well (100 to 180 meter deep) water supply constructed since 1900 had been reported. Out of about 1 lakh population, 40 thousands people in 37 villages were affected. 427 cases of skin cancer were found in study population of 7500 persons. The prevalence of Blackfoot disease was 8.9 per 1000 in the study population.

In the South East part of Hungary, drinking water wells were contaminated with arsenic in concentration high enough to pose long term health hazard to about 4 lakh persons. Such contamination was believed to be arising from leaching of rocks containing arsenic by the percolating water.

Arsenic had been found to be accumulated in the soils of extensive areas of Audcan mountains between Argentina and Chila. Calginatong furnaces from a refinery in Taroku

village on the Island of Kyushu in Japan started leverating arsenite and Sulpher Dioxide during 1920. The environment was so polluted that people almost from every house was found sick.. It was only in 1971 that the Toroky Expsode was known and in year 1973 , adequate steps were taken to stop the furnaces.

In North of Chile, arsenic occurred naturally. Weathering of rocks and volcanic eruptions caused arsenic pollution to air, water and food. Endemic contamination of fresh water supply through leaching of arsenic wastes from mining operation to spring water was also reported in Argentina. Concentration of arsenic above permissible limit in ground water had also been reported in some parts of New Zealand.

The reported results of drinking water samples from Utah, Alaska, Chile (Antofagasta), Taiwan, and Nova Scotia intended to find the total arsenic and arsenic compounds, are given in Table-6.

Table -6 : Total Arsenic, Arsenite, and Arsenate Concentrations in Drinking Water Samples (Source : Irgolic, 1986)

Location	Concentration in mg As/L as			Arsenite
	Total As	Arsenite	Arsenate	Arsenate
Hinckley, UT	0.18	0.01	0.17	0.06
Delta, UT	0.02	0.01	0.01	1.00
Barefoot	3.10	2.40	0.70	3.40
Mauer	4.5-6.0	0.4-4.60	0.1-4.3	1.00
Antofagasta				
Untreated	0.75	0.016	0.740	0.02
Taiwan	1.10	0.024	1.08	0.03
Nova Scotia 1	8.0	4.50	3.50	1.30
Nova Scotia 2	0.63	0.31	0.32	1.00

Arsenic pollution in ground water/atmosphere has been a problem in many countries. The affected countries required decades to ascertain the exact cause of the pollution. Even if the remedial measures were not well defined to get rid of arsenic pollution.

9.2 ARSENIC MENACE IN INDIA

In India, occurrence of arsenic in ground water was first reported in some parts of West Bengal in year 1978. During 1980, the cases of arsenical dermatosis were reported in the

4 districts, namely; North 24 Paraganas, South 24 Paraganas, Nadia & Murshidabad. Upto year 1993, the problems of arsenic pollution in ground water were reported to be in 6 districts, namely; Malda, Murshidabad, Nadia, North 24 Paraganas, South 24 Paraganas and Bhurdaman, covering 149 mouzas, 6 non mouzas and 3 municipalities with affected population of about 0.96 million (SOES, 1994). According to the survey made up to 1995, about 757 mouzas, 9 non municipal/outer growth areas and 9 municipalities in 56 blocks of 7 districts in West Bengal with 3.83 million population have been reported to be affected with contamination of arsenic in the drinking water supplies derived from ground water sources. While, till February, 1997, it was reported (The Statesman, 1997) that arsenic affected area has increased to 8 districts (in which some parts of Calcutta is included) comprising 57 blocks, 830 villages, and about 4.5 million people have been reported to be exposed to arsenic contamination. The growth rate of arsenic contaminated areas is shown in Figure - 4.

Occurrence of arsenic as pollutant in ground water has been reported in a linear track extending from Katiachak block of Malda district through the eastern part of Murshidabad, Nadia, eastern fringe of Bardhaman district to North 24 paraganas district with a local enclave in Sonarpur-Baruipur area of South 24 paraganas district (Figure-3). The distance between the extreme two arsenic points, i.e., block Manikchak and Joynagar in South 24 paraganas, is about 470 Km. Hoogli district is also reported to be affected by arsenic (SOES, 1996). Among the all districts, Malda, Murshidabad, Nadia, North 24 paraganas and South 24 paraganas are located to the east of the river Bhagirathi, whereas, Bardhaman and Hoogli districts are located to the west of the river Bhagirathi. The concentration of arsenic was reported to be varying from 0.052 to 3.2 ppm, with an average of 0.2 ppm. Table-7 and also the map given in Fig. 3 represent the areas, and range of reported contamination level of arsenic pollution in ground water.

The overall survey reports upto May, 1994 and January, 1996 (SOES) (Table-8) show that more than 175,908 people in 37 blocks in six districts ,and 200,000 people in 50 blocks in seven districts were arsenic affected respectively , which later on reported to be increased to 450,000 people in 57 blocks in 8 districts by the end of Feb., 1997

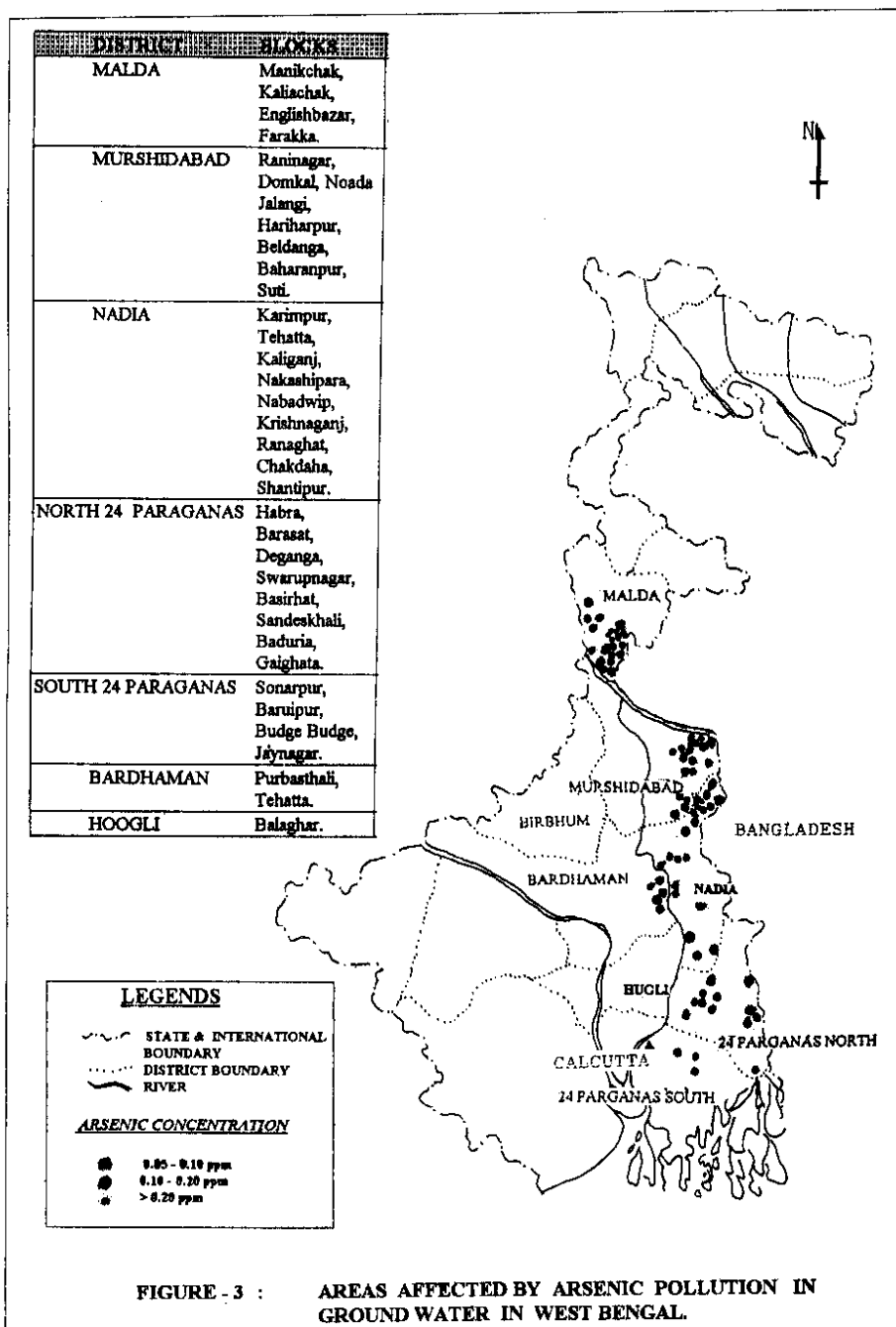


Table -7 : Districts and Areas Affected by Arsenic Pollution

DISTRICT	BLOCKS	Value of Arsenic in ppm.
MALDA	Manikchak, Kaliachak, Englishbazar, Farakka.	0.055 - 1.434
MURSHIDABAD	Raninagar, Domkal, Noda Jalangi, Hariharpur, Beldanga, Baharanpur, Suti.	0.05 - 0.90
NADIA	Karimpur, Tehatta, Kaliganj, Nakashipara, Nabadwip, Krishnaganj, Ranaghat, Chakdaha, Shantipur.	0.055 - 1.0
NORTH 24 PARAGANAS	Habra, Barasat, Deganga, Swarupnagar, Basirhat, Sandeskhali, Baduria, Gaighata.	0.06 - 1.28
SOUTH 24 PARAGANAS	Sonarpur, Baruipur, Budge Budge, Jaynagar.	0.06 - 3.20
BARDHAMAN	Purbasthali, Tehatta.	0.10 - 0.50
HOOGLI	Balaghar.	-

Ground water in deltaic area of Baghirathi basin extending eastwards towards Bangladesh has also been reported severely affected by arsenic pollution. A total number of 34 districts out of total of country's 64 districts are reported to be under the grim of arsenic concentration above WHO's recommended value of 0.05 mg/l. More than 38% of the tested

samples showed concentrations above 0.05 mg/l. Approximately, 65,000 sq. km area covering population of 51 million has been reported to be arsenic affected (The Statesman, 1997).

The sources arsenic pollution in ground water in Bangladesh had also been described similar as in West Bengal. Pollution threat of arsenic in ground water both in West Bengal and Bangladesh has been exaggerated in the same ground water basin.

Report shows that the contamination in ground water in West Bengal was first observed in year 1980, however, at that time the severity of arsenic could not be visualized as it is today or as reported since last 5/6 years. A yearwise menace of arsenic-affected areas are given in Table- 9.

Table - 8 : Survey report of arsenic -affected upto May,1994 & January, 1996

	Upto May 1994	Upto January 1996
Total area	34,344 km ²	37,493 km ²
Total population	30,184,038	34,632,024
Total no. of blocks/PS	144	162
Total no. of arsenic-affected blocks/PS	37	50
Total population of arsenic-affected blocks	7,896,387	9,562,898
No. of arsenic-affected villages/wards	312	560
Approx. population drinking arsenic-contaminated water above 0.05 mg/l	>804,422	>1,100,000
Approx. population showing arsenic-related skin manifestation	>175,908	>2,20,000

The reported occurrence of arsenic beyond permissible limit i.e., more than 0.05 mg/l are all confined within meander belt zone of the upper deltaic plain comprising the Late Quaternary sediments. It has been established beyond doubt that water of the intermediate (second) aquifer is polluted with arsenic. Neither the shallow (first) aquifer nor the deep (third) aquifer has reports of As in ground water. In some places, contamination of arsenic are also reported at a deeper aquifer (250 m. to 260 m.). It is interesting to note that concentration of arsenic is more pronounced in the intermediate depth ranging 20m. - 80m.

The ground water in arsenic infected zone is reported to be characterized by high Iron, Calcium, Magnesium and Bi-carbonate with low chloride, sulphate and flouride. The pH was everywhere reported to be greater than 7. The sand grains in the arsenic-infected aquifer were obtained generally coated with iron and arsenic-rich material.

Table -9 : Survey report of arsenic-affected districts, blocks, villages in West Bengal (From January 1990 to Feb., 1997)

Year	Districts	Blocks	Total no. of villages
1990	South 24-Paraganas Murshidabad	Baruipur Raninagar-II Domkal	7
1993	South 24-Paraganas North 24-Paraganas Nadia Burdawan Murshidabad Malda	Bhangor -I Barasat-I, Barasat-II, Habra-I, Habra-II, Deganga, Swarupnagar, Basirhat, Baduria, Gaighata Harighata, Chahdaha, Shantipur Nabwadip, Kaliganj, Tehatta-I, Tehatta-II, Karimpur-I/II Purbasthali-I, Purbasthali-II Beldanga, Baharampur, Nowda Hariharpara, Raninagar-I, Suti-II Kaliachalk-I, Kaliachalk-II, Kaliachalk-III, Englishbazar, Manikchalk.	330
May, 1994	South 24-Paraganas <i>(In addition to the districts reported in year 1992)</i>	Sonarpur	13
August, 1995	South 24-Paraganas Murshidabad <i>(In addition to the districts reported in year 1994)</i>	Joynagar, Magrahat-II Suti-I, Farakka, Bhagabangola-II Murshidabad, Raghunathganj-II	116
January, 1996	South 24-Paraganas Hugli <i>(In addition to the districts reported in year 1995)</i>	Bhangor-II, Budge Budge-I, Budge Budge-II, Bishnupur-I Bishnupur-II Balagarh	94
Feb., 1997	Parts of Calcutta		
TOTAL	8 DISTRICTS	57 BLOCKS	830 VILLAGES

9.3 SOURCES OF ARSENIC IN GROUND WATER IN W.B.

The problem of arsenic pollution in ground water in West Bengal has been reported to be due to the geological formations of the source materials. Occurrence of iron-pyrite and the change of geo-chemical environment due to over-exploitation of ground water or excessive

fluctuation of ground water table have been thought to be the reason of decomposition of pyrites to ferrous sulphate, ferric sulphate and sulphuric acid.

Kinniburgh et al., (1994) while explaining the groundwater quality of London basin aquifers, mentioned that due to high ground water withdrawal, the pyrite (FeS_2) oxidised, and the acid released during oxidation of pyrite reacted with minerals, leading to high concentrations of cations in the pure water. Welch et al., (1988) reported that mobilization of arsenic in sedimentary aquifers may be in part, a result of changes in the geochemical environment due to agricultural irrigation. In the deeper subsurface, elevated arsenic concentrations are associated with compaction caused by ground water withdrawal.

The SOES (1996) made an estimate of arsenic withdrawal from a single Rural Water Supply Scheme (RWSS) supplying water to few villages in Jothgopal, Malda which indicates that 147.825 kg of arsenic came out in one year. Since the arsenic of such huge proportion could not be anthropogenic, the source of arsenic is considered to be *geological*.

The sand and clay deposited at shallow level by the Ganga-Bhagirathi river system in the late Quaternary period are originally enriched in arsenic and iron-bearing minerals, derived from trap and granitic source rock.

Use of heavy duty pumps for irrigation in the arsenious zone had also been reported and thought to be helped in mixing of waters in the isolated arsenious pockets in the aquifer, leading to progressively wide incidence of arsenic contamination. Another factor suspected to be a contributing factor to the occurrence of high concentration of dissolved arsenic in parts of 20m - 70 m aquifer is percolation of water downward through the oxidation zone resulting towards enrichment of dissolved oxygen that may help oxidation of the arsenic in the arsenious layers to HAsO_4^{2-} anion which is soluble in the prevailing mildly alkaline ground water in that zone.

9.4 FEATURES OF ARSENIC POLLUTED WATER

- *Iron concentration is high,*
- *pH values are higher, indicating alkaline nature of water,*
- *Water quality is mainly of Bi-carbonate type,*
- *Chloride concentration in arseniferous groundwater is relatively lower than the normal chloride concentration of water of the shallow zone of the respective areas,*
- *Sulphate concentration in groundwater is also relatively lower than the normal sulphate concentration of the area,*
- *The ground water in arsenic infected zone can be characterized by high Calcium, Magnesium with low sulphate and flouride.*

10.0 HYDRO-GEOLOGICAL CONDITIONS OF AFFECTED AREAS

The area affected by the arsenic pollution falls both under upper delta and lower delta regime of the Bhagirathi/Hooghly drainage system (Fig. 1). The arseniferous belt is confined within the meander belt zone of both the upper and lower delta plains. The hydrogeological condition of the affected districts are as follows:

10.1 Malda District

The area lies to the West of Mahananda river and Barind upland and South of Kalindi river having gentle slope towards south and is underlain by the unconsolidated quaternary sediments. Ground water in this part occurs under unconfined to semiconfined condition. The flow of the ground water is south and south west. Average variations of water table are between 5.20 to 6.5 m over the year. Average seasonal fluctuation of water level varies from 0.83 to 1.13 m for the period from January to April and from 1.47 to 2.76 m for the period from April to November.

10.2 Murshidabad District

The area lies to the east of Bhagirathi river and forms a part of upper delta region, having flat and gentle slopes from north to south and is underlain by quaternary to recent sediments. Ground water in this part is under unconfined condition. The flow of ground water

is generally towards south. Average variation of water table are between 2.00 m to 2.80 m over the year, whereas, average seasonal fluctuation of water level varies from 0.59 to 1.41 m for the period from January to April and from 2.24 m to 3.03 m for the period from April to November.

10.3 Nadia District

The area lies between the upper and lower delta region of Bhagirathi/Hoogly drainage system. Ground water in the area occurs under unconfined condition. There is a general south-easterly gradient of the water table. The gradient is steeper in the northern and north-western parts. Water level fluctuation varies from 1-2 metres. Average seasonal fluctuation of water table in the area varies from 0.74 to 1.78 m for the period from January to April and from 2.00 to 3.16 m for the period from April to November. The flow of ground water is towards south and south-east.

10.4 North 24 Parganas District

The area form a part of lower delta region and is nearly flat with regional slope towards south. Ground water in the area occurs under unconfined condition having flow direction towards south-east. The average fluctuation of water table is between 2-3 m. Average seasonal fluctuation of water table in the area varies from 0.78 to 2.04 m for the period from January to April and from 1.46 to 4.14 m for the period from April to November.

10.5 South 24-Parganas District

The area forms a part of lower delta region and is nearly gentle slopping towards south and is underlain by a thick pile of quaternary sediments. Ground water in this area occurs under semi-confined to confined condition. The average fluctuation of water table is between 0.65 to 2.10 m. Average seasonal fluctuation of water table in the area varies from 0.59 to 1.50 m for the period from January to April and from 1.19 to 2.47 m for the period from April to November. The flow of ground water is towards south-east.

10.6 Bardhaman District

The area lies in the western marginal part of the delta region of Bhagirathi/Hoogly drainage system and is underlain by the quarternary to recent sediments. Ground water in this part occurs under water table condition. The average fluctuation of water table is between 4.5 to 5.85 m over the year. Average seasonal fluctuation of water level varies from 0.59 to 2.04 m for the period from January to April and from 1.19 to 4.14 m for the period April to November. The flow of ground water is towards east.

11.0 HYDRO-CHEMISTRY OF GROUND WATER

General symptoms of arsenic contaminant ground water have been discussed in section 9.4. District-wise features of arsenic contaminant water are discussed below:

11.1 Malda District

Ground water in this area is slightly alkaline in nature as pH value varies from 7.09 to 7.32. Concentration of arsenic and iron found to be varied from 0.055 ppm to 1.434 ppm and from 0.05 ppm to 6.88 ppm respectively. The ground water is reported to be hard. Concentration of sulphate and chloride are reported to be low.

11.2 Murshidabad District

Ground water in the area is slightly acidic to alkaline in nature with pH value varying from 7.7 to 8.2. Concentration of arsenic and iron varies from 0.04 to 1.86 mg/l and from 0.05 to 0.5 mg/l. respectively. Ground water in the area is reported to be hard. Sulphate and chloride concentration are reported to be low. From the litholog test conducted by CGWB following test results of chemical analysis had been reported:

Table - 10 : Results of Chemical Analysis for Murshidabad District

Depth range	As	Fe	pH	K	Cl	HCO ₃	SO ₄
	(All values except pH are in mg/litre)						
Shallow (15-15.6 m)	0.04- 0.08	0.05- 0.25	7.7- 8.2	2.7- 4.8	3.55- 30.1	91- 525	<1
Intermediate (34.5-42 m)	0.08- 0.68	0.4- 0.5	7.9- 8.2	4.8- 5.8	7.1- 14.0	451- 567	<1
Deep (72 -78 m)	0.0- 1.86	0.2- 0.25	7.9- 8.2	3.9- 19.0	3.55- 14.0	482- 518	<1

11.3 Nadia District

Ground water in the area is almost neutral to alkaline in nature with pH value varying from 6.92 to 8.20. Concentration of arsenic and iron varies from 0.02 to 0.2 mg/l and from 0.01 to 4.80 mg/l. respectively. Sulphate and chloride concentration are reported to low. Results of chemical analysis of water samples for some blocks are reported below:

Table - 11 : Results of Chemical Analysis for Nadia District

Depth range	As	Fe	pH	Cl	HCO ₃	K	SO ₄
	(All vales except pH are in mg/litre)						
Shallow (13.8 - 15 m)	0.1-	3.9-		14-	281-	2.3	<1
	0.2	4.8	7.6	57	371		
Intermediate (40.8-52 m)	0.02-	0.01-	8.2	11-	268-	2.5-	<1
	0.2	0.7		21	408	5.6	
Deep (73.5 -90m)	0.00-	0.01-	8.2	7.1-	268-	5.6-	<1
	0.2	0.84		14	415	6.6	

11.4 North 24-Parganas District

Ground water in the area is almost neutral to alkaline in nature with pH value varying from 6.95 to 7.86. Concentration of arsenic and iron varies from 0.02 to 0.38 mg/l and from 0.9 to 4.5 mg/l. respectively. Ground water is hard and concentration of sulphate and chloride are low. Results of chemical analysis of some bore holes samples are reproduced below:

Table - 12 : Results of Chemical Analysis for North 24 Parganas District

Depth range	As	Fe	pH	Cl	HCO ₃	K	SO ₄
	(All values except pH are in mg/litre)						
Shallow (13.8 m)	0.02	1.36-	7.3-	7.0-	-	-	-
		4.9	7.4	8.8			
Intermediate (37.3 -39.3 m)	0.02-	1.89-	7.5-	7.0-	-	-	-
	0.38	4.5	7.7	12.4			
Deep (108 - 117 m)	Nil	0.90-	7.3-	8.8-	-	-	-
		3.38	7.4	10.6			

11.5 South 24-Parganas District

Ground water in the area is neutral to alkaline in nature with pH value varies from 6.91 to 7.59. Arsenic and iron concentration varies from 0.06 to 3.20 ppm and from 0.70 to 18.0 ppm respectively.

11.6 Bardhaman District

Ground water in the area is neutral to alkaline in nature with pH value varies from 7.0 to 7.6. Concentration of arsenic and iron varies from 0.01 to 0.50 ppm and from 2.6 to 6.8 ppm respectively. Concentration of chloride and sulphate are low. Ground water in this area is hard.

12.0 CORRELATION OF PARAMETERS IN ARSENIC CONTAMINANT WATER

A statistical study was carried out by the Central Ground Water Board, Calcutta to establish the correlation between different chemical parameters in the arsenic contaminant water. The objectives of study were to; i) find out inter-relationship of As with Fe, chloride, sulphate and total hardness, and ii) predict As content of the water in terms of Fe and chloride.

A general positive correlation between arsenic and iron contents was noted in the arsenic contaminant water of South and North 24-Parganas districts. The correlation of arsenic with chloride, sulphate and hardness were reported to be less. Correlation amongst parameters was found improving when arsenic values were log-transformed (i.e., $\log As \times 10^3$) Whereas, for chloride the correlation was moderately negative.

The correlation matrix of different parameters obtained from $n = 19$ are reproduced below:

	$\log (As.10^3)$	Fe	Chloride	Sulphate	Hardness
$\log (As.10^3)$	1.000				
Fe	0.294	1.000*			
Chloride	- 0.491*	- 0.321	1.000		
Sulphate	0.021	- 0.422*	0.481*	1.000	
Hardness	- 0.214	0.021	0.769*	0.261	1.000

* At 90% confidence level.

The positive correlation of arsenic with iron has been described to be used to compute for arsenic concentration in terms of iron content (in mg/l) of water from the fairly efficient quadratic regression equation as given below:

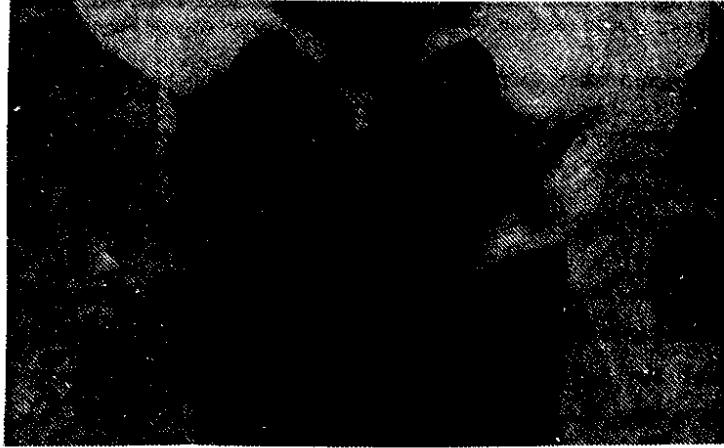
$$[\text{As}] = 1.33561 + 0.25442 [\text{Fe}] - 0.01353 [\text{Fe}]^2$$

12.1 Impact of Aquifer Performance Test

Plots in Figs. 5 represents the variation of arsenic concentration obtained from the chemical analysis of pumping test conducted at different places for a continuous period of 8 hours. The other chemical parameters were found to be withdrawn at a constant rate.

13.0 TOXICOLOGICAL AND EPIDEMIOLOGICAL ASPECTS OF ARSENIC POLLUTION

Chronic arsenic intoxication can lead to gastro-intestinal disturbances, hyperpigmentation and peripheral neuropathy. Studies had shown that both trivalent and pentavalent inorganic arsenic compounds in solution are readily absorbed after ingestion. Most of the inhaled and deposited arsenic are absorbed from either the respiratory or gastro-intestinal tract. Except in rats, in other animals and in men, most inorganic arsenic is eliminated at a much higher rate mainly via the kidneys. In both animals and human being exposed to trivalent arsenic in a single dose the initial elimination is about 75% in the urine and a few percent in the faeces during the first week. In case of pentavalent arsenic the elimination is 80-90% for a single dose during first 2 days. However, the differences increase with increasing dose levels. The toxic effects of arsenic ions can be attributed to their high reactivity with sulph hydri-containing enzymes, arsenate ions appear to replace phosphate ions in metabolic processes as the arsenate ion is isosteric and iso electronic with phosphate. Symptomatology or arsenical toxicity develops insidiously after six months to two years or more depending on the amount of intake of arsenic laden groundwater and arsenic concentration in the water sample. Darkening of skin (diffuse melanosis) in the body or in palm is the earliest symptom. Not necessarily that people suffering from arsenic toxicity will have symptom of diffuse melansis. Photographs 1 & 2



Photograph - 1 : Pigmentation in hands due to the consumption of arsenic contaminated water. (Photograph of hands of a person from arsenic affected area, village: Getuaghachi, Nadia District, West Bengal).



Photograph- 2 : Spotted melanosis on the back.
(Photograph of back of a person from arsenic affected area, village : Getuaghachi, Nadia District, West Bengal).

show the effect of consumption of arsenic polluted water on the skin of persons in Gethuagachi, in Nadia district in West Bengal.

- * *Darkening of skin (diffuse melanosis) in the body or in palm is the earliest symptom.*
- * *Spotted pigmentation (spotted melanosis) is usually seen on chest, back or limbs.*
- * *The symptoms of chronic arsenic poisoning include various types of dermatological lesions, muscular weakness, liver disorder, paralysis of lower limbs, etc.*
- * *Urine is suitable indicator medium for assessment of exposure to inorganic arsenic.*

When nutrition is poor or when inorganic arsenic is present in excess in the diet or drinking water, and in habitation of biomethylation occurs, the levels of arsenic in the blood rise and the tissues may be bathed in inorganic arsenic. At high chronic doses arsenic gets deposited and bounded to tissues such as skin, lung and hair. Elimination of arsenic, in both animal and man, takes place mainly via kidneys. Arsenic levels in the hair of unexposed human adults are usually below 1 mg/kg.

Acute and sub-acute effects of arsenic may involve many organ system including respiratory, gastro-intestinal, cardiovascular, nervous and haematopoietic system. Early signs include weakness, languor, anorexia, nausea and vomiting with diarrhoea and constipation. As arsenic poisoning progresses, symptoms become more characteristic and include diarrhoea, edema, skin pigmentation and hyperkeratosis. At later stages, signs of hepatic, renal, erythropoietic and nervous system involvement become evident. Most of the reported chronic arsenic exposure in humans focused on the dermal disorders. These lesions are considered to be pre-cancerous and may develop into skin cancer. Exposure to inorganic arsenic can cause skin cancer, mainly of low malignancy.

- * *The Organic arsenic forms are known to be less toxic than inorganic arsenic forms.*
- * *Arsenic causes internal cancer. The US-EPA viewed that the form of skin cancer induced by arsenic is treatable, and observed that not all forms of cancer are equally lethal.*
- * *The US-EPA stressed that all forms of arsenic does not equally carcinogens.*

14.0 STATE OF ART FOR ARSENIC REMOVAL

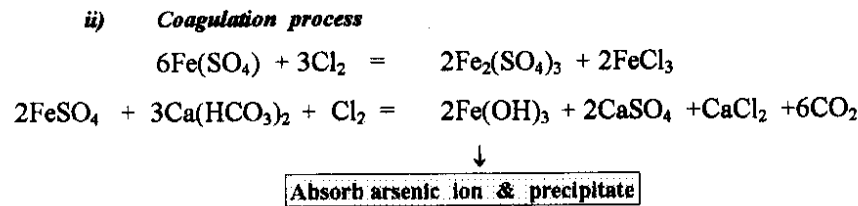
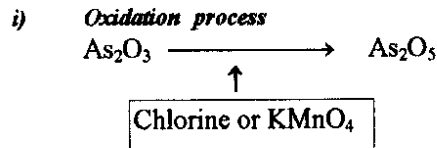
Several methods are in practise for removal of arsenic from aqueous solution. Out of them, the three main techniques are ; i) Reagent precipitation, ii) Sorption on inorganic compounds, and Ion exchange on polymeric resins.

14.1 Reagent Precipitation

The reagent precipitation is the most widely practiced method for removal arsenic from groundwater.

The process is similar to the traditional coagulation process used in water treatment. The treatment process comprises oxidation of trivalent arsenic to pentavalent one either by Chlorine or Potassium permanganate.

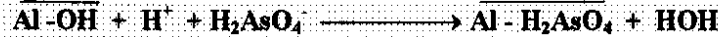
After oxidation the water is treated in a clarifier where ferric chloride or ferric-sulphate is used as coagulant. This coagulant precipitates ferric-hydroxide which ultimately adsorbs the arsenic ion. The process is dependent on pH of the system. It was reported that 95% removal of arsenic takes place between pH range 5 to 8.5. It was also further reported that As(+3) is not effectively removed by iron coagulants. So oxidation of As(+3) to As(+5) is a pre-requisite for removal of arsenic. Thus arsenic removal process involves removal of As(+5) only. 98% of As(+5) can be removed by iron coagulation under pH range of 5.5 to 8.5. The removal process can schematically be represented as given below:



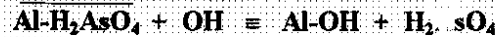
14.2 Sorption on Inorganic Compounds

Activated alumina is used as adsorbent for this technique. The basic mechanism for adsorption of arsenic by activated alumina is protonation and deprotonation as illustrated below:

Adsorption of Arsenite



Desorption of Arsenate



Under acidic condition activated alumina adsorbs the arsenic ion. Above pH 8.2, activated alumina does not adsorb arsenic ion because of cationic exchange form. Thus, above pH 8.2, significant removal of arsenic through adsorption is hardly possible. At low pH (less than 4) activated alumina dissolves in acid and as such removal efficiency is impaired. It was reported that at pH 6, optimal arsenic removal can be obtained. Apart from activated alumina, activated charcoal and bone-charcoal are also practiced for arsenic removal. However, granular activated carbon is efficient for arsenic removal. Bone-Charcoal is less efficient than the activated alumina process. Hathaway *et al.* (1987) conducted a pilot plant study for activated alumina and ion exchange method for removal of arsenic from drinking water source. Outcome of their studies are reported below:

Treatment method: activated alumina with pH adjustment:

Raw water was treated in a downflow, packed-bed configuration. Before placing in the treatment vessel, the raw water was adjusted to pH 5.5 using a dilute solution of sulfuric acid (H_2SO_4). Higher/lower value of pH in the effluent was adjusted by the adjustment of influent pH value.

Treatment method : activated alumina with no pH adjustment

The method was identical to the method as above except that the adjustment of pH which was only made during the neutralization step after regeneration. Backwash and regeneration was also same as for method above except that the acid feed adjustment of pH to

2.5 that used to be terminated when effluent pH dropped to 9.0. The pH was not adjusted further until the neutralization phase of the next regeneration was initiated.

It was observed that at pH 9.0-9.1, activated alumina is ideal for silica removal but unfavourable for arsenic removal.

14.3 Ion Exchange on polymer Resins

The process is similar to the principle of adsorption process. Strong base anionic exchange resins in chloride form can be used as ion exchange polymeric resin. Removal of As(+5) was best achieved by the activated alumina system with adjusted pH of 5.5 by sulphuric acid. This process has got some limitations in the sense that the background competing ions interfere the exchange process to a considerable extent. It was reported that with high TDS (over 500 mg/l) and sulphate content 25 mg/l, the ion exchange does not work efficiently. Ion-exchange process always need pre-treatment as the particular matter may plug the resin media and impede the flow of water. Besides that, biological growth may form under the operation condition. Thus, ion-exchange process is always preceded by a pre-treatment process which makes the system cumbersome and costly.

Ion-exchange technique have mostly been appreciated in the laboratory scale. Known to be a latest technique, "Polymer Binding and Membrane Separation" though not practiced in large scale but removal efficiency has been reported to be very encouraging.

Hathaway et al. experimented the performance of Ion -exchange with no pH adjustment and observed that use of strong-base anion exchange resin was inefficient for arsenic (+5) removal because of the competition of the high sulfate concentration.

14.4 APPROPRIATE LOW COST TECHNOLOGY

The techniques discussed above for arsenic removal are quite useful when these are used in smaller scale. For use in larger scale, as it would be required for arsenic removal from ground water in West Bengal, the above mentioned techniques would be very costly and would

be difficult to afford even by the Government where water is supplied at free of cost, as in India. On the other side, in countries like India, most of the rural areas have no organized water supply schemes and people in those areas are largely depend on supply of shallow tube wells or hand pumps. It is, therefore, necessary to look into an appropriate low cost technology for arsenic removal which is less costly and easily affordable. The Public Health Engineering Department, Govt. of West Bengal, All India Institute of Hygiene and Public Health (AIIH & PH), School of Tropical Medicines, Calcutta, and School of Environmental Studies (SOES), Jadavpur University have developed appropriate methodologies for removal of arsenic from water withdrawn from under-ground water. These are described below:

14.4.1 ARSENIC REMOVAL PLANT FITTED DIRECTLY WITH HAND PUMP

The Public Health Engineering Directorate, Govt. of West Bengal has developed this technique. Works based on the adsorption technique and function under continuous flow system. Arsenic removal plant can be attached with the hand pump. The bed materials of such unit are activated carbon, silicious material and activated alumina. The adsorption mechanism is controlled at low pH for maximum efficiency of arsenic removal.

14.4.2 CO-PRECIPITATION-SEDIMENTATION-FILTRATION-UNDER CONTINUOUS FLOW SYSTEM

Since arsenic $3+$ can not be removed without adsorption, it is required to oxidise $As(+3)$ to $As(+5)$ and co-precipitate it. Such methodology has been developed on the principle of co-precipitation of arsenic with the help of ferric chloride, multimedia filtration with sand and activated alumina which ensure 99% removal of arsenic. An oxidizing agent is required to be added initially before co-precipitation.

14.4.3 DOMESTIC FILTERS

All India Institute of Hygiene and Public Health, Calcutta has developed this technique for arsenic removal in a domestic scale. Methodology is based on coagulation-flocculation - sedimentation and filtration process. Alum dose is necessary for the arsenic removal. Control of pH is necessary. Generally pH in range between 7 & 8 is considered to be ideal. A

minimum detention time of 30 minutes prior to filtration is reported to be essential. One hour detention prior to would be ideal. Uses of ferrous sulphate, ferric chloride, aluminium sulphate, lime as alum were reported to have satisfactory performance. School of Tropical Medicines (STM) had also reported satisfactory performance of using domestic filter.

School of Environmental Studies (SOES), Jadavpur University, Calcutta had developed another type of domestic filter for removal of arsenic. Such filters are generally fitted with specially manufactured candles. Tablet of chemicals developed by SOES need to be added for removal of arsenic. Method for disposal of arsenic-adsorbed candles had been reported successful for arsenic removal.

15.0 CRITICAL ANALYSIS OF THE PROBLEMS

The problem of arsenic pollution in groundwater in West Bengal has been reported to be grim and described as the World's biggest calamity. Over the years, the rate of victims and spreading of arsenic contamination in ground water have been multiplied. Tables- 8 & 9 and Fig. 4 represent a qualitative pictures of arsenic menace in West Bengal. Sources of arsenic pollution have been described of geological origin, and it has been doubted that existence of arsenic containing iron-pyrite material in the ground water aquifer could be the reason of arsenic pollution. Over exploitation of ground water for that matter the variation of ground water table might have activated the process of hydrolysis of source materials and propagated the contaminated water towards the down gradient areas. There were no genuine evidences or scientific explanations about the occurrence of arsenic pollution, and their propagation in the ground water. Researchers based on the preliminary investigation had claimed that source could be of geological origin. Reasons of such clarification seemed to be logical, if one look into the arsenic affected areas which were observed in pocket-wise in different spells, and there exists no linearity in the concentration of arsenic over the gradient of flows. It is interesting to note that the propagation of arsenic contaminated water is more pronounced in the intermediate zone of depth range varying from 25m to 50 m. In the deeper aquifer i.e., in the confined zone, there was hardly any reported risk of arsenic pollution. The other interesting

feature of arsenic contaminant water is the positive correlation with iron content in water. Higher the concentration of iron, more the risk of arsenic pollution was observed.

Mandal *et al.* (1996) reported that very poor people and children having malnutrition food are mostly affected by arsenic. Genetic component for the inter-individual response could be the reason for such clinical manifestation.

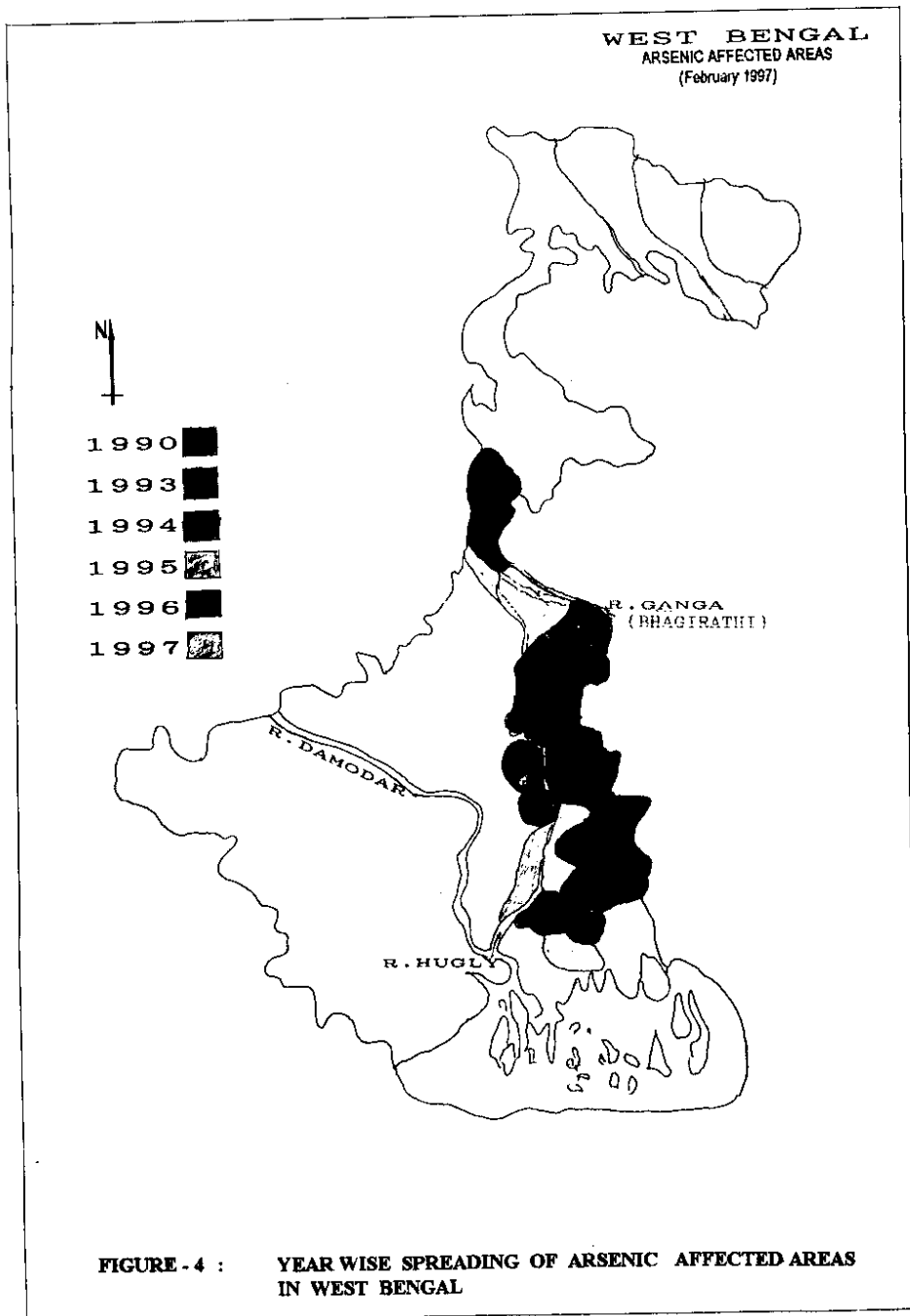
Figures 3 & 5 respectively represent the arsenic affected areas in West Bengal and the gradient of ground water flows in the affected areas. It is apparently evident from figs. 3 & 4 that spreading of arsenic affected areas occurred in pocket wise and do not show any sign of linearity of spreading in the direction of ground water flow. On the otherhand, there exist no linearity in the occurrence of arsenic concentration in the spreaded areas. That eventually reflect that sources are not in one location, and there are chances of number of sources.

It is known that billions of litres of water have been and are being pumped out every year from the arsenic affected belt with the help of ground water structures (Table-13).

Table -13 : Ground water structures operating in arsenic affected alluvial belt in W.B.

Specifications	Heavy/medium duty tubewells	Shallow tubewells	Tubewell with hand pump
Depth range	50 to 200 m	30 to 100 m	10 to 200 m
Tapping zones	30 m	10 m	3 to 5 m
Drawdown	6 to 12 m	3 to 6 m	Insignificant
Discharge	100 m ³ /h	20 m ³ /h	Small
Use	Irrigation/water supply	Irrigation/water supply	Domestic water supply
Number	About 3000	About 100000	Over 500000

Except during the rainy season (June to September), irrigation pumps are run for a few hours almost daily to irrigate the nearby fields. Pumping for eight hours per day is common. On an average an irrigation pump runs for about 500-800 hours a year. Water supply tube wells, however, run throughout the year. Mallick and Rajagopal (1996) observed that supply of oxygen to the groundwater increases with excessive variation of ground water table caused by



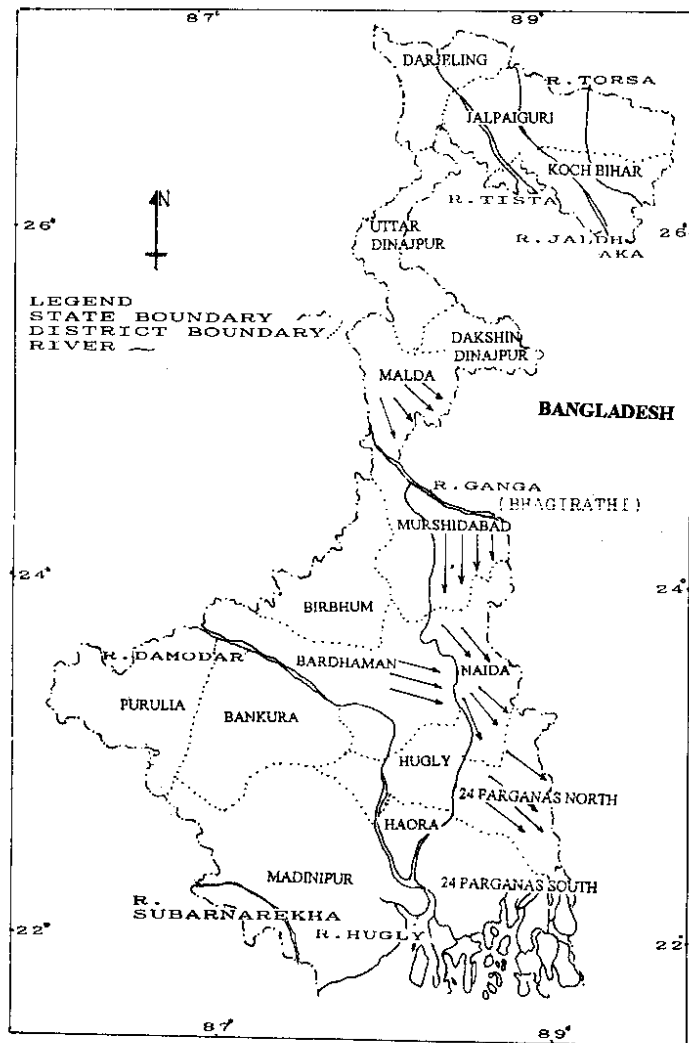


FIGURE - 5 : GROUND WATER FLOW DIRECTION IN ARSENIC AFFECTED DISTRICTS (Qualitative diagram).

oxygen to the groundwater increases with excessive variation of ground water table caused by the operation of tube wells which may cause extension of vadose zones, i.e., unsaturated air-water mixed zones (ZS). It was further suggested by them that the release of arsenic is more in and around the areas where increased supply of oxygen/dissolved air is available and is reacting with the arsenic-bearing formation. The average ground water movement has been reported to be in the order of 500 cm per year in horizontal direction and still less as per as vertical movement is concerned.

Chemical analysis data of some pumping test conducted for a period of continuous 8 hours at different locations in the arsenic affected areas reveal almost a constant drawal of arsenic constituents from ground water (Fig. 6). That eventually tell upon that more the use of arsenic contaminated waters for consumption purposes, more would be the consumption of arsenic. Figure-7 represents an indicative of arsenic consumption per capita/day for different consumption rate of water at different locations in the arsenic affected areas. For example, for the people at the Raninagar area in the Murshidabad District, if a person consumes 7.5 litres of waters in a day, he will consume 5.4375 mg of arsenic in a day i.e., 1984.68 mg As in a year. Whereas, as per the permissible limit of of Indian standard i.e., 0.05 mg/l, a person can have 0.375 mg As with the 7.5 litres of water. The amount that are in excess being consumed by the people of Ranigang areas are; $(0.725 \text{ mg/l} - 0.05 \text{ mg/l}) = 0.675 \text{ mg/l}$. Or in otherwords, a pump having yielding rate of 35 m³/hour is operated for 8 hours in a day, the amount of arsenic withdrawal from that area would be 203000 mg/day. Can one imagine the inputs of toxicity that may consume by a person? Are not the problems grave? Questions come; what are the solutions and how can get rid of the problems? What are the scientific answers?

Some interesting remedial measures had been suggested by Mallick and Rajagopal (1996). These were:

- i. *Recharge of arsenic-free rainwater,*
- ii. *Arsenic removal plants as suggested by SOES, JU,*
- iii. *Discouragement in exploiting the deeper aquifer.*

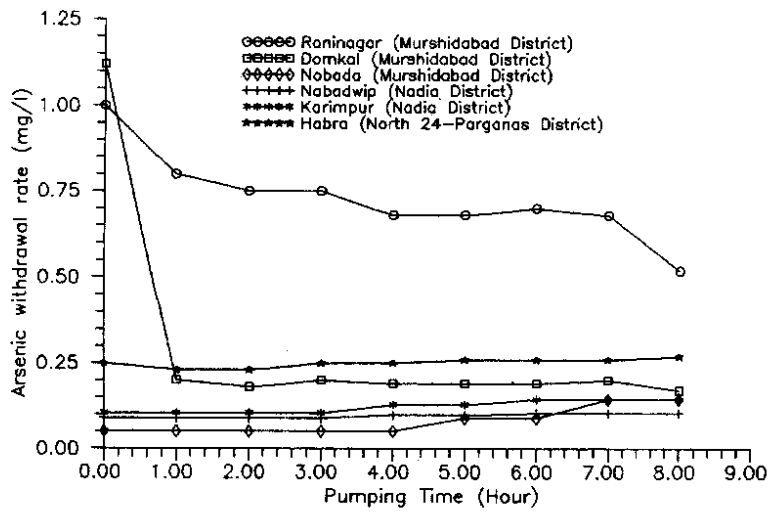


Figure - 6: Withdrawal of arsenic from groundwater at different locations.

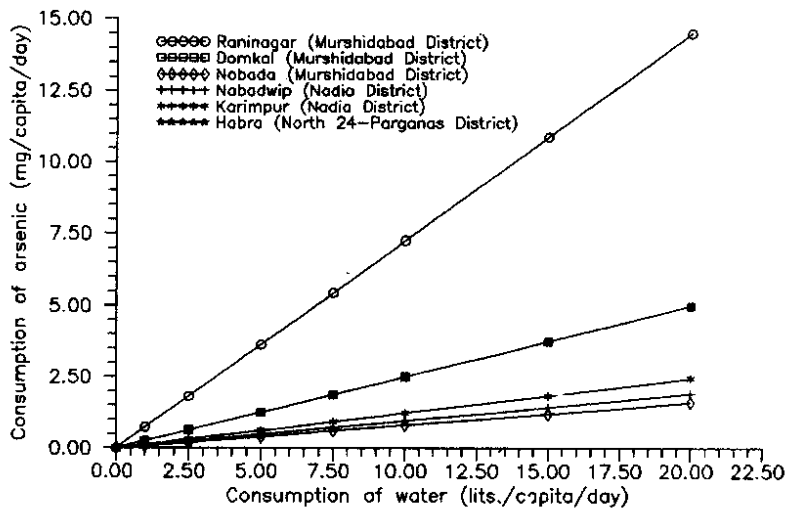


Figure - 7 : Consumption of arsenic with drinking water by people at different Districts of affected areas.

i. Recharge of arsenic-free rain water : Authors had argued that every year about 4 m of aquifer water column, on an average, is recharged at the top of the summer water table. This is equivalent to about 50 cm of rainwater amounting to half a million m³ of water per sq. km area. This huge amount of water is arsenic -free. If one can get this recharged water mixed with the shallow aquifer, say within 50 m of depth and also withdraw this water annually, then mitigation will start. For this purpose, future tubewells of all duty has to be restricted to a depth of 50 m, so that these act as underground mixing tools as well as tubewells for the purposes that they are being used now. This suggestion has the limitation on mixing mechanism which was assumed to be from arsenic-leaching.

Idea seems to be very interesting. However, the authors have not considered the possibility of occurrence of arsenic bearing material in the Vedose zone and the mixing phenomena of ground water aquifer during the various temperate conditions. Because of concentration gradient between contaminant water and pure water which is most likely through recharge, there remains chance of vertical diffusion. Doubt persists whether the proposed 50 m pure water barrier will remain as 50 m or it will change. Answer to all these questions can only be obtained after proper scientific study and mathematical modelling.

ii. Arsenic removal system : Suggested extensive use of domestic filters alongwith tablets.

This can be applied for drinking water as it is usually being done for regular filtering of water in many areas.. It may not be well appreciated when used for filtering of water require for other domestic uses, if cost effectiveness is compared.

iii. Discouragement in exploitation of deeper aquifer : The authors had argued that exploitation of deeper aquifer may lead to leaching of contaminant layer and may also be very costly affairs.

As per our National Water Policy, "adequate drinking water facility is to be ensured to the entire population both in urban and rural areas". Therefore, supply of appropriate water quality is mandatory for the Government. If alternate sources of water or appropriate remedial measures to protect the unconfined aquifer are not available, one has no options but to withdraw water from deeper aquifer even at a higher cost.

Answers to the above questions can only be gathered after a proper scientific study.

The State West Bengal receives about 2000 mm of rain every year. A proper watershed management in conjunction with management of ground water can be one of the solutions. Identification of source(s) and control of source in a scientific and logistic manner can be another line of thinking. Proper scheduling of groundwater withdrawal based on the regular monitoring of water table and ground water quality can provide a realistic estimate of ground-water balance. Correct picturization of ground water flow defining the well head protection zone or development of hydrological barrier to arrest the movement of contaminant plume from the zone of arsenic oxidation- could be other approaches for management of growing problems.

However, at the outset, following immediate remedial measures are suggested:

- * *Exploitation of ground water, in places having pockets of iron-pyrites, should be stopped,*
- * *Over exploitation of ground water should not be encouraged as it may lead to the change of geo-hydrology of the area,*
- * *Groundwater of deeper aquifer (depth below 150 m) have less risk of contaminated by any toxic substances, and hence recommended for use as drinking water,*
- * *Withdrawal and use of water from shallow aquifer should be avoided particularly for drinking purposes,*
- * *Leakage of aquifers should be so regulated that there should not be large-scale vertical leakage of water from one layer to the other,*

- * Preliminary treatment of water, atleast making use of alum, is necessary to make the water germ free,
- * In places where ground waters are thought to infected by any toxic substances, uses of near by surface water sources available round the year, if any, after proper treatment for drinking water supply may be used,
- * In absence of any surface water sources, it would be mandatory to treat arsenic infected ground water,
- * Performance of domestic filters for removal of arsenic developed by All India Institute of Hygiene and Public Health, Calcutta, in collaboration with School of Tropical Medicine, Calcutta, and School of Environmental Studies, Jadavpur University, Calcutta, have been reported in fulfillment of the drinking water requirement for small family. Use of domestic filters in arsenic affected areas may be encouraged,
- * For large scale piped water supply schemes, it is essential to design arsenic elimination plant. Activated alumina has been reported as most effective method for arsenic removal,

- * Pure water and nutritious foods are the best medicines for getting cured from arsenic poisoning (Anandabazar Patrica, August 24, 1996).

Recommended nutritious foods are :

Emblic myrobalan, Kamranga (a kind of sour fruit common in India), Pomelo, Karamcha (a kind of sour fruit), Vegetable like carrots, Seeds of Jackfruit, Soyabean, Meat, and Eggs etc.

- * River's, Pond's and Tank's water usually does not contain arsenic , hence, recommended for domestic uses (after adequate treatment)
- * Green vegetables store arsenic in the leaf . Irrigation water, if contaminated by Arsenic have the risk of contaminating vegetables. Therefore, vegetables should be properly washed with fresh water before cooking.

16.0 CONCLUDING REMARKS

Arsenic pollution in ground water in West Bengal is not new problem. Many places in the World had witnessed the menace of arsenic pollution in water, however, the problems in West Bengal can be described as the World's biggest calamity of arsenic pollution. The rate

of spreading of arsenic affected areas and reported cases of arsenic affected people are so faster that immediate control and management are necessary.

The main sources of arsenic is natural environment that eventually, due to various natural calamity and natural phenomena, transfer to the different transport media. With the passage of time, arsenic forms compounds of different bearing material and get settled or transported by natural processes into the geological formation.

Over exploitation of source material changes the chemical formation through oxidation, and propagates in the transported medium. Excessive fluctuation of ground water helps in activation of source material and the ionic arsenic get into the migration pathways of ground water flow domain.

The chemistry of arsenic pollution in ground water is not well defined, and the hydrodynamic of migration pathways is even more complicated. Number of arsenic removal techniques are available, however, the cost-effectiveness of those techniques in the context of treating ground water of such huge quantities needs to be examined.

A proper watershed management in conjunction with ground water quality modelling with objectives to find out the rate of spreading and identification of safe zone of drawal of waters, possibility of creating hydraulic barrier to arrest the spreading of contaminant water can give the answers to the future fate of the problems.

17.0 DEFINITION OF TERMS

$\mu\text{g/l}$: "micro grams per litre" means the concentration at which 1 millionth of gram is contained in a volume of 1 litre.

ppm. : "parts per million"
mg/l

$$= \frac{\text{mg/l}}{\text{Specific gravity of liquid}}$$

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**WATER IS LIFE
BUT
BECOMES CURSE
WHEN
CONTAMINATED BY
ARSENIC.**

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