MODELING OF ARSENIC TRANSPORT IN GROUNDWATER USING MODFLOW

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE
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IN
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SUBMITTED BY
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UNDER THE ESTEEMED GUIDANCE
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CERTIFICATE

This is to certify that the project report entitled **"MODELING OF ARSENIC TRANSPORT IN GROUNDWATER USING MODFLOW"** being submitted by **PHURAILATPAM SUPRIYA (Roll No. 3451)** is a bonafide record of her own work carried under my guidance and supervision in partial fulfillment for the award of the degree of Master of Engineering in Environmental Engineering from Delhi College of Engineering, Delhi.

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Dated: **(Phurailatpam Supriya)**

ABSTRACT

Arsenic contamination in the groundwater is increasing at an alarming level with time and more areas are becoming contaminated. At least 28 million people currently drink water containing more than 50 μg/l of arsenic and many more consume water with > 10 μg/l of arsenic. Evidence of chronic arsenic toxicity is accumulating and includes melanosis , hyperkeratosis of palm and sole, gangrene and skin cancer.

A MODFLOW based three-dimensional model has been simulated to understand the movement of water and arsenic in the study area situated in the Yamuna Sub-basin, West Bengal. Microbial reduction of iron oxyhydroxide (FeOOH) and release of its sorbed arsenic load to solution is an important mechanism by which arsenic enters groundwater. Arsenic pollution does not arise from oxidation of sedimentary sulphides nor from ion-exchange with phosphorus derived from fertilizer (or other sources).

MODFLOW was run for the study area and the movement of water in the study area was simulated. It was seen that the variation of hydraulic heads was more in clay than in sand layer.

Arsenic was assumed to be injected continously at a well 12005m away from both the western and northern side of the Yamuna Sub-basin in the block of Chakdah, Nadia district at a depth of 25m from the ground level. Simulation was performed for the movement of arsenic for every 1 year for a stretch of 20 years. The spatial and temporal distribution of arsenic was studied through contours maps for 1, 5, 10, 15, and 20 years. The concentration of arsenic vs time graph was also drawn. It was seen that arsenic was spreading more in the sand layer than in the clay layer, affecting more and more places near the study area.

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CHAPTER 1

INTRODUCTION

1.1 GROUNDWATER

Groundwater is a vital natural resource for the economic and secure provision of drinking water, and plays a fundamental role in human well-being. Groundwater is a significant source of drinking water in many parts of the world. Groundwater may be visualized as occurring in a subsurface reservoir, the boundaries of which are formed by adjacent less permeable or impermeable geological materials. The reservoir may be open everywhere to the land surface (unconfined), or it may be capped in large part by impermeable or relatively impermeable geological materials (confined).

Well-protected groundwater is safer in terms of microbiological quality than water from open dug wells and ponds. However, the pressure on groundwater, in terms of both quantity and quality, has increased to an extent whereby not only drinking water sources but also sensitive ecosystems are threatened by contamination through human exploitation. Increasing demand for water, a growing use of pesticides and fertilizers, atmospheric deposition and numerous point sources of contamination constitute a threat to the quality of groundwater.

1.2 GROUNDWATER CONTAMINATION

The occurrence of groundwater contamination and quality of groundwater has become major issues since some decades. Environmental contamination of groundwater due to extensive use of fertilizers, pesticides in agriculture and toxic chemicals in industry and in manufactured products has magnified the toxicity for plants, animals and society. Contaminants that can dissolve in groundwater will move along with the water, potentially to wells used for drinking water. A combination of moving groundwater and a continuous source of contamination can, therefore, pollute very large volumes and areas of groundwater. This presence and the transport of contaminants constitute a potential threat to human health and ecosystem.

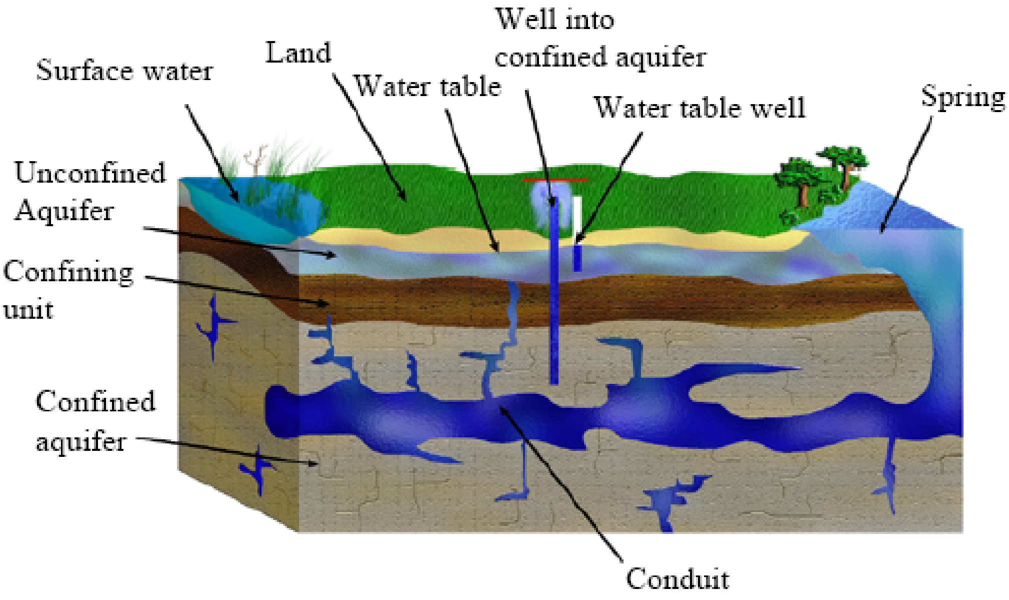


Fig. 1.1 A schematic Aquifer (*After Florida Geological Survey*).

1.3 GROUNDWATER REMEDIATION

Groundwater remediation is a process for cleaning up or containing contamination. Remediation technologies are used when there is significant risk from chemical exposure to either human health and/or the environment. Such remediation methods are designed to prevent or minimize impacts to human or environmental receptors by treating air, soil or water pathways to remove contamination with a chemical or mechanical process.

Remedial technologies work to remove a chemical(s) from the soil, air or water pathways by either of the following two ways:

(1) Breaking down the chemical(s) into a less toxic chemical such as enhanced bioremediation and thermal oxidation.

(2) Reducing the concentration of the chemical(s) to a level that is not considered toxic to humans or the environment such as pump-treat methods, soil-vapour extraction, air-stripping etc.

1.4 GROUNWATER MODELING

A groundwater model is a mathematical tool designed to represent a simplified version of the physical, chemical and biological processes taking place in a real field site. It is generally, a computer-based approximation of observed groundwater behavior. Groundwater modeling requires the development of as good a simplification of the geometry, aquifer properties and source / sink terms of the system as is achievable. The first parts of the modeling involve developing a groundwater model that adequately simulates the groundwater flow observed in long term monitoring. The second phase of model development is to couple the groundwater flow model with a pair of contaminant transport models.

1.5 ARSENIC CONTAMINATION OF GROUNDWATER

Arsenic in groundwater and its fate and transport in the environment have become matters of great concern in Bangladesh, India and several other countries. Arsenic contamination in the groundwater is increasing at an alarming level with time and more areas are becoming contaminated. Arsenic pollution of groundwater in the Bengal Basin was known about in the late 1980s and, although overlooked by a later survey, is now known to be one of the World’s worst disasters affecting humans. At least 28 million people currently drink water containing more than 50 μg/l of arsenic and many more consume water with > 10 μg/l of arsenic. Evidence of chronic arsenic toxicity is accumulating and includes melanosis (abnormal black brown pigmentation of skin), hyperkeratosis (thickening) of palm and sole, gangrene and skin cancer. Arsenic is a cumulative position in the human system and depending on the level of contamination it could take 5 to 20 years for a person to show these symptoms of sickness.

The human consequence of the pollution has been described as the worst mass poisoning of a population in history. The regulatory limit of arsenic for Bangladesh, India, UK and USA was 50ppb. But the discovery that there are adverse effects of continuous chronic exposure led WHO to lower their recommendation to 10ppb.

1.6 OBJECTIVES OF THE STUDY

The Present study has the following objectives:

1. To simulate water and arsenic movement using a 3D solute transport model.
2. To study variation of hydraulic heads of the groundwater in the Yamuna sub-basin using MODFLOW.
3. To study distribution and movement of arsenic in the groundwater of Yamuna sub-basin in West Bengal, when it is assumed to be injected continuously at a point using MT3D.

CHAPTER 2

LITERATURE REVIEW

2.1 GROUNDWATER CONTAMINATION

The term contamination means an unusual concentration of something whilst the term pollution means an unusual concentration that leads to environmental harm. Groundwater flows at a slow rate, through rock and soil formations. The soil contains high levels of carbon dioxide, which dissolves in the groundwater. This turns the groundwater into a weak acid capable of dissolving substances that neutral water cannot. Groundwater then can dissolve many of the pollutants placed in the earth and carry them downward to contaminate the groundwater.

Despite groundwater's important function to society, these resources have generally not been provided with adequate protection (*Foster et al. 2002*). Cleaning and restoring contaminated groundwater is often technically problematic and costly, and finding alternative sources for water supply is not always possible (*Lindström et al. 1995*).

Vulnerability assessment provides a basis for initiating protective measures for important groundwater resources and will normally be the first step in a groundwater pollution hazard assessment and quality protection, when the interest is at the municipal or provincial scale (*Foster et al. 2002*).

All groundwater resources are not valued equally though, and the willingness to protect a groundwater resource depends on several issues, such as the actual use of groundwater, the potential for future water supply, alternative for water supply, and the importance of the groundwater resource for sensitive ecosystems and landscapes (*Scharp et al. 1997*).

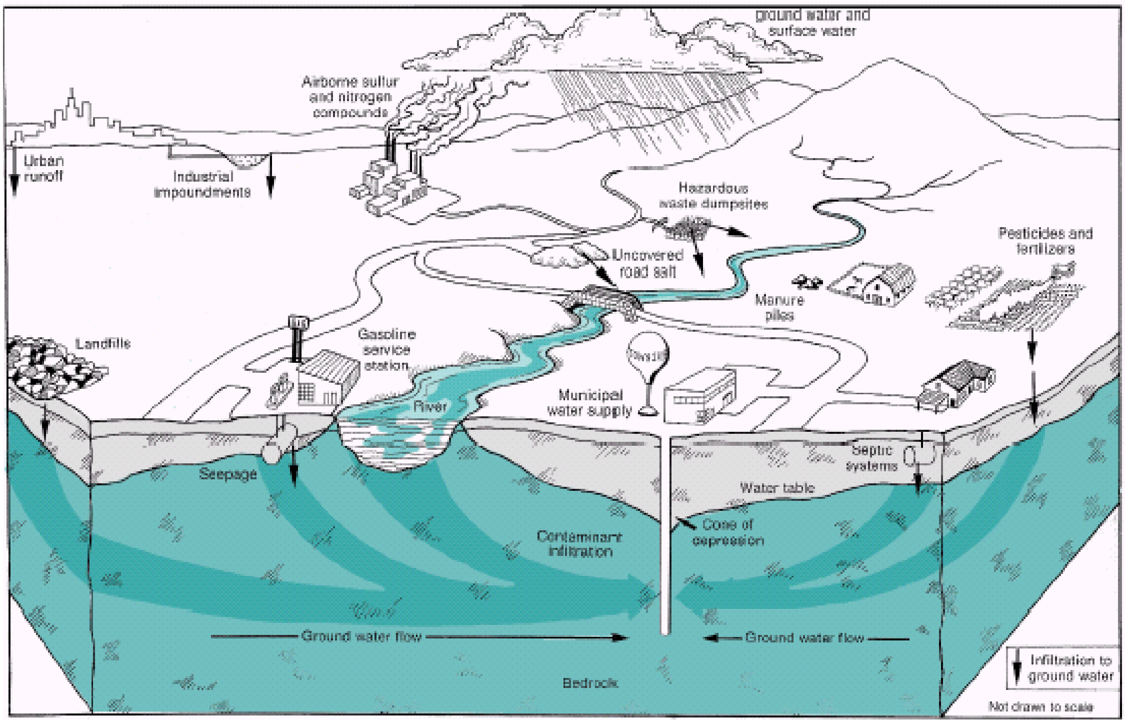


Fig. 2.1 Groundwater contamination through various processes.

Ideally, contamination of groundwater should be prevented by controlling potential contaminants, in order that they may not come in contact with groundwater. Groundwater contamination occurs through various processes and with many compounds.

2.2 ARSENIC CONTAMINATION OF GROUNDWATER

2.2.1 Arsenic - General Information

Arsenic is a silver-grey brittle, crystalline (hexagonal, rhombic), metallic-looking substance that exists in three allotropic forms (yellow, black, and grey). Arsenic is the twentieth most abundant element in the earth's crust. Arsenic is a naturally occurring element. Pure arsenic is a grey metal-like material, which is usually found in the environment combined with other elements such as oxygen, chlorine, and sulphur. Arsenic combined with these elements is called inorganic arsenic. Arsenic combined with carbon and hydrogen is called organic arsenic.

Physical Properties	Values
Atomic Number	33
Molecular Weight	74.92
Valence	3.5
Boiling Point	Sublimes at 612 °C
Melting Point	817.0 °C at 28 atm
Vapour Pressure	1.0mm Hg at 372 °C
Density / Specific Gravity	5.727 at 14 °C

Table 2.1 Physical properties of arsenic.

The two primary forms of arsenic in water are trivalent arsenic (As+3, arsenite (III)) and pentavalent arsenic (As+5, arsenate (V)). Arsenic as a free element (0-oxidation state) is rarely encountered in natural waters. Soluble inorganic arsenate (+5-oxidation state) predominates under normal conditions since it is thermodynamically more stable in water than arsenite (+3 oxidation state). Arsenic +3 tends to be more toxic than arsenic +5 (*Irwin et al. 1997*). Arsenic is listed by the US Environmental Protection Agency as one of 129 priority pollutants.

Arsenic is a chemical that is widely distributed in nature and principally occurs in the form of inorganic or organic compounds. Inorganic compounds consist of arsenite, the most toxic forms and arsenate the less toxic forms. Exposure to inorganic compounds may occur in a variety of ways through certain industrial effluents, chemical alloys, pesticides, wood preservative agents, combustion of fossil fuels, occupational hazards in mining and dissolution in drinking water. The most commonly found arsenic compounds in drinking water are trivalent arsenite or pentavalent arsenate. Organic forms of arsenic compounds occur primarily in seafood obtained from several marine organisms.

2.2.2 Arsenic Contamination of Groundwater in India

Arsenic contamination have been reported from many parts of the world such as Australia, New Zealand, Chile, Taiwan, Mongolia, India, China, Thailand, USA, UK as well as Bangladesh. But in terms of severity of the problem, Bangladesh tops the list, followed by India and China (*Harun-ur-Rashid et al. 1998).*

In India, arsenic is of geological nature originating from the natural aquifers. For India, it is generally held that rocks containing arsenic eroded from the Himalayas and deposited in the Gangetic plains later got buried in the sediments over thousand of years. These arsenic-bearing sediments form parts of the aquifers that are presently being tapped for water resources. Arsenic may be released in the groundwater by reduction of the iron oxy-hydroxides by reducing microorganisms.

Millions of people are affected by arsenic in West Bengal. Bihar has also reported cases of arsenic contamination of groundwater. Recent unconfirmed reports point to the presence of arsenic in Tamil Nadu and other states of India, implying industrial contamination of groundwater *(SEA 2001).* The problem has also been reported recently from Kaurikasa area, Chhattisgarh. Some fear that the manifestation may contaminate Seonath river and groundwater, endangering well-populated townships like Drug, Rajnandgaon and Raipur.

2.2.3 Arsenic Contamination of Groundwater in West Bengal

Arsenic pollution of groundwater in the Bengal Basin was known about in the late 1980s (*Guha Mazumder et al. 1988, PHED 1991*) and, although overlooked by a later survey (*BGS 1992*), is now known to be one of the World's worst disasters affecting humans. At least 28 million people currently drink water containing more than 50 μg/l of arsenic, and many more consume water with > 10 μg/l of arsenic (*Dhar et al. 1997*; *Ullah 1998*; *Mandal et al. 1998; DPHE 1999, 2000*). The human consequence of the pollution has been described as the worst mass poisoning of a population in history (*Smith et al. 2000*).

Arsenic was detected in 8 out of 18 districts of West Bengal stretching from Malda in the North and South 24 Parganas on the other end (*De 2003*).

Sl.No.	**Physical Parameters**	**West Bengal**
1.	Area in sq. km.	89193
2.	Population in million (according to 2001 census)	80
3.	Total number of districts	18
4.	No. of arsenic affected districts (groundwater arsenic above 50µg/l)	9
5.	Total number of water samples analyzed	115000
6.	% of samples having arsenic > 10µg/l	50.3
7.	% of samples having arsenic > 50µg/l	25.1
8.	Area of arsenic affected districts in sq. km.	38865
9.	Population of arsenic affected districts in million	50
10.	Number of arsenic affected Blocks / Police Station	75
11.	Number of arsenic affected villages (approx.) where groundwater arsenic is above 50µg/l	3500
12.	Total hair, nail, urine, skin-scales samples analyzed	25000
13.	Arsenic above normal level (average) in biological samples.	89%
14.	People drinking arsenic contaminated water above 50µg/l (approx.) in million	6
15.	People screened for arsenic patients (preliminary survey)	86000
16.	Number of registered patients with arsenic skin manifestations*	8500 (9.8%)

* Very preliminary survey *(after Nath, 2003)*

Table 2.2 Extent & magnitude of arsenic problem in West Bengal.

2.2.4 Harmful Effects of Arsenic

Chronic exposure to arsenic has been linked to serious medical conditions, including a variety of cancers (*National Research Council 1999*). A review of studies conducted in other parts of the world shows that between 16% and 21%of the exposed subjects develop disease due to arsenic toxicity (*SEA 2001*). Inorganic arsenic compounds are known to be human carcinogens based on sufficient evidence of carcinogenicity in humans (*IARC 1987*). The toxic effect of arsenic species depends mainly on their chemical form, route of entry, age, sex, doses and duration of exposure. Arsenic toxicity occurs through contaminated food or drinking water.

Skin diseases are the most common effects of arsenic poisoning. Long-term exposure to excessive arsenic causes changes in skin pigments and hyperkeratosis; promotes development of ulcerations of skin; and accelerates the risk of cancer in liver, bladder, kidney and skin. It happens in three stages:

- Initial stage: Dermatitis, Keratities, Conjunctivitis, Bronchitis and Gastroenteritis.
- Second stage: Peripheral Neuropathy, Hepatopathy, Melanosis, Depigmentation and Hyperkeratosis.
- Final stage: Gangrene in the limbs, Malignant Neoplasm, and Cancer.

2.2.5 Determing Exposure to Arsenic

Urine can be tested for arsenic up to a week after the exposure. Arsenic can also be measured in hair and fingernails within a few months of exposure. The results of arsenic urine tests may be misleading if you have eaten seafood, marine fish or ocean-derived vitamin supplements in the past five days. If a person suspect's high arsenic exposure, tests that monitor the functioning of the liver and kidneys should be done. A doctor on blood samples can do these tests.

2.2.6 Theories of Arsenic Mobilization

Three mechanisms might explain arsenic pollution of groundwater in the Bengal Basin, *viz:*

1) Arsenic is released by oxidation of arsenic-bearing pyrite in the alluvial sediments (*Mallick et al. 1996*; *Mandal et al. 1998*);

2) Arsenic anions sorbed to aquifer minerals are displaced into solution by competitive exchange of phosphate anions sourced from over-application of fertilizer to surface soils (*Acharyya et al. 2000*);

3) Naturally-occurring arsenic that is sorbed to iron oxyhydroxides (FeOOH) is released when the iron oxyhydroxide is reduced as anoxic conditions develop during sediment burial (*Bhattacharya et al.1997; Nickson et al. 1998; McArthur et al. 2001; Ravensrof et al .2001)*

(1) Pyrite Oxidation and Irrigation Drawdown

Oxidation of pyrite is envisaged to happen as irrigation draws down the water table allowing oxygen into previously anoxic aquifer sediments. This theory is rejected because of the following arguments. A relation between the distribution of arsenic pollution and that of irrigation is therefore be expected, yet a comparison of the two shows they bear no relation to each other: indeed, the distributions appear antipathetic. This geographical evidence does not support the existence of a causal link between arsenic pollution and tubewell irrigation. The distribution of maximum dry-season water table lowering is also antipathetic to the pattern of arsenic pollution. Other reasons for rejecting pyrite oxidation as a mechanism are as follows. The sediments contain too little arsenical pyrite for this mechanism to be important. Measured sulphur concentrations in aquifer sediments represent both pyritic and organic sulphur but allow upper limits to be placed on pyrite abundance of 0.3% (*Nickson et al. 2000*), 0.02% (AAN 1999) and 0.06% (*DPHE 1999*). Were arsenic to be released by partial oxidation of arsenical pyrite, Bangladesh groundwater's, which are anoxic, would have an iron/sulphate molar ratio of 0.5 from the stoichiometry of the reaction:

$$2FeS_2 + 7O_2 + 2H_2O = 2Fe^{2+} + 4H^+ + 4SO_4^{2-} \qquad (2.2.1)$$

In reality, iron and sulphate are mutually exclusive in solution, as are arsenic and sulphate; arsenic concentrations > 50 µg l^{-1} occur only where sulphate concentrations are < 30 mg l^{-}. If oxidation was complete and FeOOH was produced, rather the Fe^{2+} that would form by partial oxidation, the arsenic would be sorbed to the FeOOH (*Mok et al. 1994*). Finally, arsenic pollution is uncommon in hand-dug wells (*Chakraborty 2001*), which are shallowest, and most exposed to atmospheric oxygen and so would be most polluted were arsenic derived from pyrite by oxidation.

Pyrite forms during early burial, either by reaction of dissolved hydrogen sulphide (from sulphate reduction) with solid FeOOH or reaction of dissolved Fe^{2+} with dissolved sulphide ions. In the former case, arsenic sorbed on FeOOH will be incorporated into the resulting pyrite. In the latter case, as iron reduction precedes sulphate reduction in the sequence of diagenetic reactions, the arsenic released by FeOOH reduction will be sequestered from solution by pyrite forming from later sulphate reduction. The presence of trace pyrite in the sediments shows that it has not been oxidized and so is not a source of arsenic in groundwater.

(2) Competitive Exchange with Fertilizer-Phosphate

The fact that the use of phosphate fertilizer in Bangladesh has increased greatly over the past 15 years has lead to suggestions (*e.g. Acharyya et al. 2000*) that the arsenic pollution may result, at least in part, from the displacement from FeOOH of sorbed arsenic as a result of competitive (anion) exchange by phosphate leached from soils after excessive use of phosphate fertilizer. This theory is also rejected. The use of phosphate fertilizer in Bangladesh is widespread but amounts used are not high by international standard. There are extensive areas of the country where groundwater is essentially free of both arsenic and phosphorus and it is in these areas that irrigation is most intense and application of fertilizer might be expected to be highest. This argument alone is sufficient to reject any link between fertilizer and arsenic. Another such argument is that waters attain a bicarbonate concentration of at least 200 mg l^{-1} before phosphorus, arsenic, or iron, are found in significant amounts (*McArthur et al. 2001*). Waters lowest in bicarbonate are the youngest and least evolved, but they would contain most phosphorus (and so arsenic), were phosphorus supplied from surface application of fertilizer.

The fact that phosphorus in groundwater cannot contribute much to arsenic pollution is shown by the experimental desorption by phosphate of arsenic sorbed to mineral surfaces (*Manning et al. 1997*). These authors showed that P/As mole partition ratios for desorption of arsenic by phosphate were around 5000. Given this ratio, no more than 2 $\mu g\ l^{-1}$ of arsenic would be desorbed by a phosphorus (as P) concentration in groundwater of 5 mg l^{-1}, the approximate upper limit for Bangladesh groundwater. Add the fact that ageing increases arsenic retention on FeOOH and it can be seen that arsenic pollution by competitive exchange with phosphorus will be negligible, whatever the sources of phosphorus.

(3) Reduction of FeOOH

Reduction of FeOOH is common in nature and has been invoked previously to explain the presence of arsenic in anoxic surface waters (*Aggett et al. 1985*) and anoxic groundwaters (*Bhattacharya et al. 1997; Nickson et al. 1998; McArthur et al. 2001*). Reduction of FeOOH (Eq 2.2.2) is a microbial process

$$8FeOOH + CH_3COOH + 14H_2CO_3 \rightarrow 8Fe^{2+} + 16HCO_3^{-} + 12H_2O \qquad (2.2.2)$$

that is driven by microbial metabolism of organic matter, particularly acetate (*Nealson 1997*) and is accompanied by microbial reduction of arsenate to arsenite (*Zobrist et al. 2000*). That reduction of FeOOH is common and intense in the aquifers of the Bengal Basin is shown by high concentrations of dissolved iron (≤ 24.8 mg l^{-1}, *DPHE 1999*); that it is accompanied by reduction of As(V) to As(III) is shown by the fact that dissolved arsenic is present overwhelmingly as arsenite. The finding of significant amounts of arsenate in Bangladesh groundwater (*DPHE 1999, 2000*) is an artifact of the storage of iron-rich waters before analysis, a procedure known not to preserve arsenic speciation (*Cherry et al. 1979*).

The spatial distribution of phosphorus in well water closely parallels that of arsenic, although the well-by-well correlation of arsenic and phosphorus concentrations is modest. This similarity of distribution points to a common diagenetic origin for arsenic and phosphorus. Both elements form anions that sorbs strongly to iron oxyhydroxide and their joint release during reduction of FeOOH probably contributes to their similar geographical distributions.

An invocation of FeOOH reduction to explain arsenic pollution needs to address why some groundwater in Bangladesh are high in iron and low in arsenic and others are low in both. Arsenic pollution and iron are absent from groundwater in aquifers of Lower Pleistocene and older age because these aquifers are oxic and, particularly where iron has been recrystallized as more stable phases such as hematite (*BADC, 1982*), reductive dissolution of iron oxyhydroxides does not occur in them.

In some coastal areas, where both shallow (<40 m) and deep (>130 m) aquifers are anoxic and contain dissolved iron, only the shallow aquifers contain pollutant arsenic. It may be that arsenic in the deep aquifer was mobilized during early diagenesis but has long since been flushed out by meteoric waters, which have been flushing the deep aquifer since well before the 18 Ka sea level minimum of around 130 m below the present level. In contrast, the Holocene shallow aquifer, largely less than 7 Ka in age, has not been so well flushed. Reduction of FeOOH will dissolve most of the surface-sorbed As(V) but not necessarily all the FeOOH, some of which may remain for later reduction. The As(V) will be reduced during FeOOH reduction (*Zobrist et al. 2000*) but not strongly re-sorbed, as As(III) sorbs less strongly to FeOOH than does As(V). A further reason why the deep aquifer is not arsenic polluted may be that sulphate reduction leads to sequestration of both iron and arsenic in diagenetic iron sulphides in the sediments, but not necessarily in the proportion in which they are seen in solution.

An invocation of FeOOH reduction to explain arsenic pollution also needs to explain why there is seldom a good relation in groundwater between arsenic and iron, or between iron and bicarbonate. The co-variance between iron and bicarbonate (expected from Eq 2.2.2) may be poor because bicarbonate is produced by reduction of nitrate and sulphate, and weathering reactions (driven by methanogenic-CO_2), not by iron reduction alone. Poor correlations of arsenic with iron may arise because of resorption (partial, as arsenite sorbs less well than does arsenate) of arsenic onto fresh FeOOH exposed by dissolution, or because the As/FeOOH ratio may vary from place to place, for example in response to differing amounts of FeOOH on mineral surfaces and differing mineral abundances. Finally, poor correlations between iron and other constituents may result from the sampling protocol used.

Filtering reduces the amount of arsenic in well water presumably because filtering iron-rich waters may remove iron from solution unless done under anoxic conditions in a glove bag. More than 50% of dissolved iron may be lost at low (1-2 ppm) concentrations. At higher concentrations, losses may be proportionately smaller but they may still be significant in terms of mass. The iron oxyhydroxide precipitated on the filter may scavenge arsenic during filtration. Rural consumers do not filter well water before use so the data for the regional survey may underestimate arsenic concentrations in waters and so the risk associated with water use.

2.2.7 REMOVING ARSENIC FROM WATER

The available treatment technologies for arsenic removal give varying results depending on the concentration of arsenic in water, the chemical composition of water including interfering particles and the amount of water to be treated. Other important considerations include the feasibility and cost of the treatment process. The commonly used biophysical methods are: coagulation, softening, iron and manganese oxidation, anion exchange, activated alumina membrane processes and elecrodialysis. But the most reliable water treatment processes for arsenic removal are: Reverse Osmosis and Distillation. Of the two processes, reverse osmosis devices are less costly, take less time, and use less energy than distillation devices. Reverse osmosis devices can be installed at the point of entry (for the entire household water supply) or for drinking water only. Treating all of the household water will be considerably more expensive than treating drinking water only.

The prohibitive cost of these technologies has prompted the search for alternative sources such as rainwater harvesting for obtaining arsenic-free water.

2.3 APPLICATIONS OF MODFLOW

MODFLOW was used to simulate steady-state flow in an aquifer and Permeable Reactive Barriers (PRB). The comparisons showed that pH profiles and anion and cation concentrations in PRBs could be predicted accurately by this method. Two common public-domain programs, MODFLOW and RT3D, were combined to form the simulator (*Li 2004*).

MODFLOW was applied to simulate groundwater flow in a three-layer conceptual model of groundwater flow in the Upper Floridan Aquifer beneath north central Florida and southwestern Georgia (*Davis 1996*). This model describes the flow directions, ascertains hydraulic boundaries and included groundwater sources via sinkholes and outflows to surface rivers.

Recent use of MODFLOW has been in the field of groundwater vulnerability assessments (*Gumbricht et al. 1996; Beverly et al. 1999; Lasserre et al. 1999; Gogu et al. 2001*).

MODFLOW was used to estimate the impact of pumping on water levels in Mason County, Illinois and the migration of conservative solutes toward the irrigation well (*Kelly et al 1999*).

MODFLOW-96 was used to simulate the impact of the injection and the different pumping operations in a piezometer. MT3D was used to simulate the movement of bromide in the model area and it was shown that the concentration decrease in bromide depends directly on the hydraulic conductivity of the aquifer (*Sánchez-Pérez et al. 2003*)

MODFLOW was used to construct a groundwater model of the Mallee areas south and west of the Murray river in South Australia and Victoria to record the recharge in the region and the salinity of the river Murray (*Barnett 1990*). Several years after this initial transient modeling exercise, the model was rerun using aerially distributed values of deep drainage, and estimates of the time lag between clearing and the increase in aquifer recharge (*Cook 1989*). This resulted in much lower predicted salts inflow in the early time periods, because of the effect of time lag.

MODFLOW was used to construct a simple slice model to simulate the increase in groundwater flow to the Murrumbidgee due to clearing in the area near Kyalite, New South Wales. It was found that there is an increase in the salt inflow due to land clearance (*Cook et al. 1996*).

The combination of MODFLOW and RT3D was used to simulate flow, transport, and geochemical reactions in Permeable Reactive Barriers (PRBs), and the predictions made with the MODFLOW-RT3D model were in general agreement with field data from PRBs (*Li 2004*).

The surface water model HSPF (Hydrological Simulation Program - FORTRAN) and the ground water flow model MODFLOW was integrated to create the Integrated Hydrologic Model (IHM) (*Andersen et al. 2000*). The IHM integration interprets fluxes across the model interface and storages near the interface for transfer to the appropriate model component, accounting for disparate discretisation of land segments in HSPF and grid cells in MODLFOW.

Algorithms from the Precipitation-Runoff Modelling System (PRMS) and the MODFLOW groundwater model was used to create a new integrated model (*Markström et al. 2002*).

CHAPTER 3

MECHANISMS AFFECTING THE SOLUTE TRANSPORT IN GROUNDWATER

3.1 DARCY'S LAW

Darcy's law is the basic law that governs the groundwater flow through the saturated zone, which states that the rate of filtration of the groundwater flow is directly proportional to the hydraulic gradient.

$$v = Ki \tag{3.1.1}$$

with

v = velocity of flow [LT^{-1}]

K= coefficient of hydraulic conductivity [LT^{-1}]

i = hydraulic gradient [-]

Hydraulic conductivity varies from 10^{-9} m/day for unfractured shale and igneous rock to 1000 m/day for gravel or cavernous limestone (*Hudak 2000*).

3.2 TRANSPORT MECHANISMS

Transport mechanisms are those mechanisms, which decide the movement of the contaminant in the aquifer. The most important mechanism affecting solute transport is Advection, Diffusion, Dispersion, Sorption and Biodegradation.

3.2.1 Advection

Advection is the movement of a solute with the flowing groundwater according to the seepage. The term convection is usually used if groundwater flow is caused by density or temperature gradients. However, both terms are not always clearly separated from each other. Advection is the transport along pathlines.

Therefore pure advective transport can be calculated immediately from results of the flow model with so called pathline models. This requires no further solution of equations or equation systems as the pore velocity u, which determines the advective flux, can be derived directly from interpolation of the known specific cell fluxes Q:

$$Q = -Ak_f I \tag{3.2.2}$$

with

A = Cross-sectional area for water flux $[L^2]$

k_f = hydraulic conductivity $[L\ T^{-1}]$

I = hydraulic gradient [-]

$$q = \frac{Q}{A} \tag{3.2.3}$$

with

q = specific flux or Darcy-velocity or filter velocity $[L\ T^{-1}]$

$$u = \frac{q}{n_e} \tag{3.2.4}$$

with

u = pore velocity $[L\ T^{-1}]$

n_e = effective porosity [-]

Analytical solutions for pathlines can be provided for simple boundary conditions and model geometry.

There are certain cases in field where an advective model provides a useful estimate of contaminant transport. Some models include the concept of arrival time by integration along known streamlines. Streamline models are used to solve for arrival times of particles that move along the streamlines at specified velocities, usually in a two-dimensional (2-D) flow net.

3.2.2 Diffusion

Diffusion is a molecular mass transport process, which causes spreading due to concentration gradients and random motion. It causes a solute to move from an area of higher concentration to an area of lower concentration. Diffusive transport can occur in the absence of velocity.

Diffusive flux is described by Ficks law:

$$J = -D_m \frac{\partial c}{\partial n} \tag{3.2.5}$$

With

J = diffusive flux [M L^{-2} T^{-1}]

D_m = coefficient of molecular diffusion [L^2 T^{-1}]

$\frac{\partial c}{\partial x}$ = concentration gradient [M $L^{-3}L^{-1}$]

Molecular diffusion is a relatively slow process. The coefficient of molecular diffusion for dissolved ions is roughly 10^{-9} m^2s^{-1}. The magnitude of diffusive transport can be estimated with the help of a strongly simplified calculation (e.g. *Neretnikes 2002*):

$$l = 2.2\sqrt{D_m t} \tag{3.2.6}$$

with

l = distance of diffusive transport for which the mean concentrations equals 50% of the maximum concentration [L]

t = typical time [T]

For liquids, the diffusion coefficient can be predicted by the Stokes Einstein equation,

$$D_m = \frac{KT}{3\pi\mu d} \tag{3.2.7}$$

with

K = Boltzmann's constant

T = Absolute temperature

μ = Dynamic Viscosity

d = Molecular diameter of diffusing substance

Diffusion is usually only a factor in the case of very low velocities such as in tight soil or clay liner, or in the case of mass transport involving very long time periods.

3.2.3 Dispersion

Dispersion is caused by heterogeneities in the medium that create variation in flow velocities and flow paths. These variations can occur due to friction within a single pore channel, due to velocity differences from one channel to another, or due to variable path lengths.

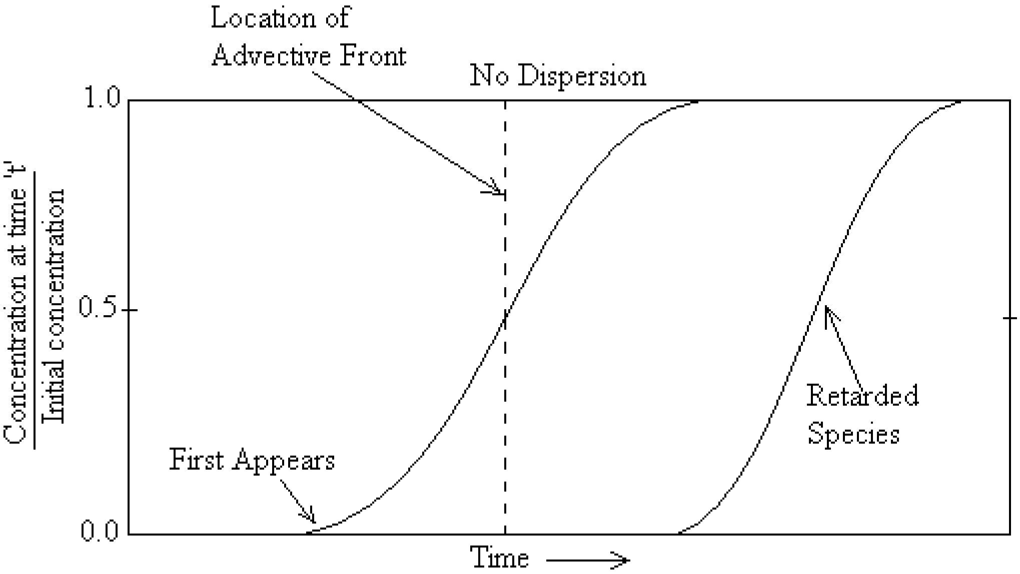


Fig. 3.1 Breakthrough curves showing effects of dispersion and retardation.

Dispersion can be described analogous to Fickian diffusion:

$$J = -D\frac{\partial c}{\partial n} \tag{3.2.8}$$

with

J = dispersive flux [M $L^{-2}T^{-1}$]

D= dispersion coefficient [$L^2 T^{-1}$]

$\frac{\partial c}{\partial x}$ = concentration gradient [M $L^{-3}L^{-1}$]

Dispersion in 2-D causes spreading in the longitudinal (x) and transverse (y) directions both ahead of and lateral to the advective front. Many typical contaminant plumes in groundwater are represented by two-dimensional advective-dispersive mechanism. Longitudinal dispersion causes spreading and decreases concentration near the frontal portions of the plume.

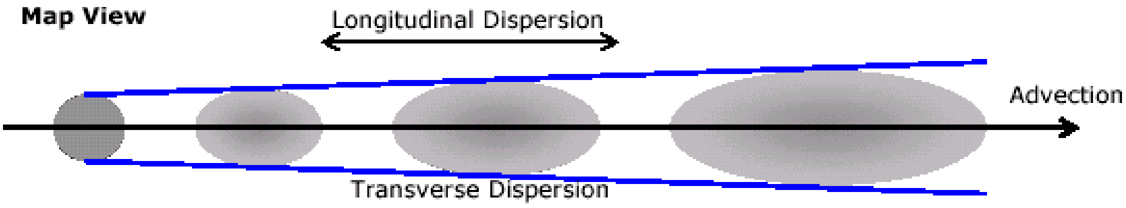


Fig 3.2 Longitudinal dispersion and Transverse dispersion.

Mechanical dispersion is a mixing process caused by fluid moving around obstruction in the flow field. As a dissolved chemical species moves through a porous media the presence of mineral soil grains cause the particles to disperse.

Hydrodynamic dispersion is the mixing process caused by different local velocities in a continuous flow domain, in which, solutes spread out and are diluted compared to simple advection alone. Within pores of a soil where flows are usually laminar there is a variation of velocity from zero at the boundary to a maximum near the pore center. Hydrodynamic dispersion is also defined as the sum of molecular diffusion and mechanical dispersion.

Like molecular diffusion, dispersion is an irreversible process. However, there are number of important differences between diffusion and dispersion:

- In general the dispersion coefficient is orders of magnitude larger than the coefficient of molecular diffusion
- Molecular diffusion is an isotropic process, whereas dispersion shows anisotropic behavior already in an otherwise isotropic ideal medium with dispersion in flow direction being always larger than transverse dispersion

- The coefficient of molecular diffusion is independent of the scale of observation, whereas the dispersion coefficient is a scaling value, i.e. it increases with increasing scale of observation
- The dispersion coefficient depends on the pore velocity. It can be calculated using the so called dispersivity α (a mixing path):

$$D = \alpha u \tag{3.2.9}$$

with

α = dispersivity [L]

u = pore velocity [L T^{-1}]

The dispersivity is a porous medium property. Its value depends on the degree of aquifer heterogeneity and on the integral transport scale. In homogeneous single grained sands the dispersivity is in the order of the pore diameter, while it may become very large in natural aquifers.

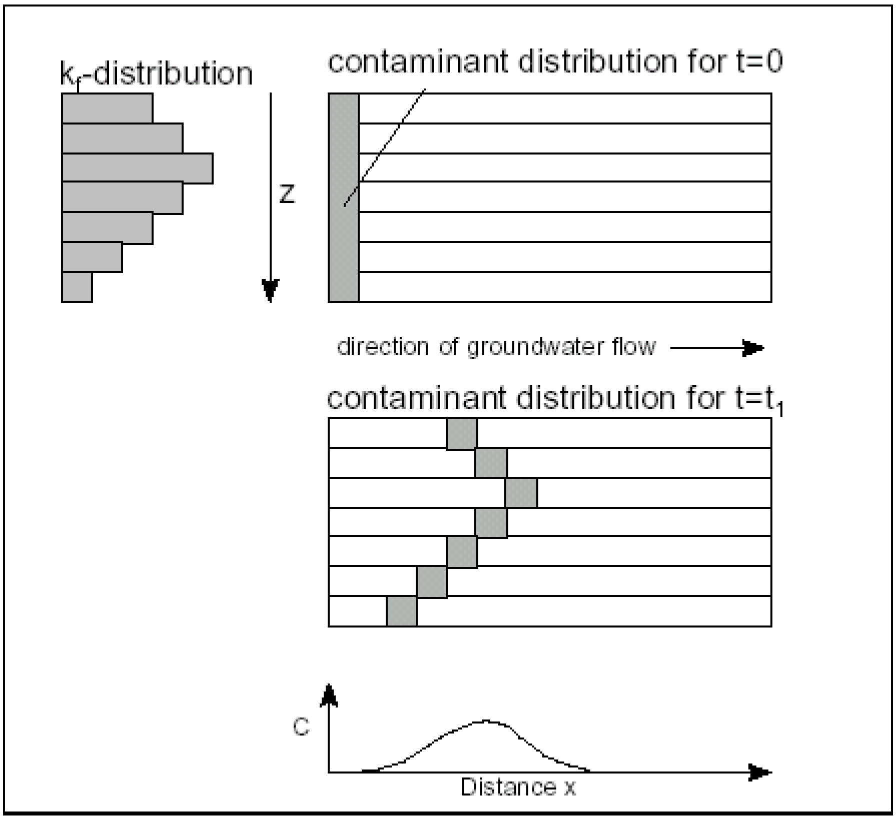


Fig 3.2 Effect of Dispersion (*after Kinzelbach, 1992*).

It can be noted that it is molecular diffusion, which finally makes up the mixing process, but dispersion increases the surface area and thus the overall diffusive fluxes.

3.2.4 Linear or Non-linear Sorption

Sorption refers to the mass transfer process between the contaminants dissolved in groundwater (solution phase) and the contaminants sorbed on the porous medium (solid phase). It encompasses two more specific process referred to as adsorption and absorption. Adsorption is the association of a contaminant with the surface of a solid particle. Absorption is the association of a contaminant within a solid particle. Sorption is an important process affecting the transport of contaminants, in the subsurface and can significantly influence the ability to remediate contaminated sites.

It is generally assumed that equilibrium conditions exist between the solution-phase and solid - phase concentrations and that the sorption reaction is fast enough relative to groundwater velocity so that it can be treated as instantaneous. The functional relationship between the dissolved and sorbed concentrations is called the sorption isotherm. Sorption isotherms are generally incorporated into the transport model through the use of the retardation factor.

Three types of sorption isotherms are considered in the MT3D transport model: Linear, Freundlich and Langmuir.

The linear sorption isotherm assumes that the sorbed concentration ($\overline{C}$) is directly proportional to the dissolved concentration (C):

$$\overline{C} = K_d C \tag{3.2.10}$$

with

K_d is called the distribution coefficient [L^3M^{-1}]

The retardation factor is defined as

$$R = 1 + \frac{\rho_b}{\theta}\frac{\partial \overline{C}}{\partial C} = 1 + \frac{\rho_b}{\theta}K_d \qquad (3.2.11)$$

The Freundlich isotherm is a non-linear isotherm, expressed in the following form:

$$\overline{C} = K_f C^a \qquad (3.2.12)$$

with

K_f is the Freundlich constant $[L^3M^{-1}]^a$

a is the Freundlich exponent [-].

Both K and a are empirical coefficients. When a is equal to 1, the Freundlich isotherm is equivalent to the linear isotherm. The retardation factor for the Freundlich isotherm is defined accordingly as:

$$R = 1 + \frac{\rho_b}{\theta}\frac{\partial \overline{C}}{\partial C} = 1 + \frac{\rho_b}{\theta}aK_f C^{a-1} \qquad (3.2.13)$$

Another non-linear sorption isotherm is the Langmuir isotherm, described by

$$\overline{C} = \frac{K_l \overline{S} C}{1 + K_l C} \qquad (3.2.14)$$

with

K_l is the Langmuir constant $[L^3M^{-1}]$

$\overline{S}$ is the total concentration of sorption sites available$[MM^{-1}]$

The retardation factor defined for the Langrnuir isotherm is then

$$R = 1 + \frac{\rho_b}{\theta}\frac{\partial \overline{C}}{\partial C} = 1 + \frac{\rho_b}{\theta}\left[\frac{K_l \overline{S}}{(1 + K_l C)^2}\right] \qquad (3.2.15)$$

3.2.5 Biodegradation

Biodegradation of contaminants refers to complete conversion of a contaminant to mineralized end products (i.e. CO_2, H_2O and salts) through metabolism by living organisms. In groundwater system, the organisms that carry out this process are bacteria indigenous to the aquifer.

The metabolism of groundwater contaminants is an extremely important process since it has the potential to impact the fate of all organic groundwater contaminants, and is a process that has the potential to yield non-hazardous products. It is a complicated fate process due to the diversity of bacteria that may be involved, and range of metabolic processes that can be expressed.

CHAPTER 4

MODELING OF GROUNDWATER CONTAMINATION

4.1 INTRODUCTION TO GROUNDWATER MODELING

In recent years groundwater modeling has become a major part of many projects dealing with groundwater exploitation, protection, and remediation. As computer hardware and software continue to be improved and become more affordable, the role of models in highly quantitative earth sciences is increasing accordingly. It is essential, however, that for any groundwater model to be interpreted and used properly, its limitations should be understood. In addition to strictly ‘technical’ limitations, such as accuracy of computations (hardware / software), the following is true for any model:

- It is based on various assumption regarding the real natural system being modeled,
- Hydrogeologic and hydrologic parameters used by the model are always just an approximation of their actual field distribution which can never be determined with 100% accuracy,
- Theoretical differential equations describing groundwater flow are replaced with systems of algebraic equations that are more or less accurate.

A groundwater model is a mathematical tool designed to represent a simplified version of the physical, chemical and biological processes taking place in a real field site. A groundwater- modeling component consists of a groundwater quantity model and a groundwater quality model. The groundwater quantity model will be used to simulate groundwater movement in an aquifer. The groundwater quality model requires the output of the groundwater quantity model to simulate pollutant movement in the ground water system.

4.2 USE OF GROUNDWATER MODELS

Groundwater models can be used as:

1. **Predictive tools**: In this, the models are used for determining future conditions or the impact of a proposed action on existing conditions in the subsurface. Predictive models are by far the largest group of models built in hydrogeologic practice.
2. **Interpretive or Research tools**: In this, the models are used for understanding system dynamics and processes.
3. **Generic or Screening tools**: In this, the models are used for the purpose of developing management standards and guidelines. These models generally incorporate uncertainty in aquifer parameters.

4.3 DEVELOPING A GROUNDWATER MODEL

A groundwater flow model can be developed with the help of the following steps:

1. Develop a **Conceptual Model** based on the physical, chemical and biological processes, which may be governing the behavior of the system.
2. Translate the conceptual model into **Mathematical Model** i.e. a set of partial differential equations and an associated set of boundary conditions.
3. If the mathematical model is solved by analytical methods, the solution is **Analytical Model**. It is possible only for simple geometric, homogeneous aquifers and simple boundary conditions.

   If the mathematical model is solved by numerical methods, the solution is **Numerical Models**.
4. If the numerical model is implemented by a computer program, it is the **Computer Model**.

Anderson and Woesser (1992) propose a modeling protocol that can be summarized as follows:

Step 1: Establish the purpose of the model.

Typical objectives may include:

(a) Testing a hypothesis or improving knowledge of a given aquifer system.

(b) Understanding physical, chemical or biological processes.

(c) Designing remediation systems.

(d) Predicting future conditions or the impact of a proposed stress on a ground water system.

(e) Resource management.

Step 2: Develop a conceptual model of the system.

These may include the following steps:

(a) Define hydrogeologic features of interest (e.g. aquifer). The conceptual model may combine several geologic formations into a single unit or may subdivide a single formation into aquifers and confining units.

(b) Define the flow system and sources and sinks of water in the system. Sources or inflows may include recharge from infiltration, recharge from surface water bodies, or artificial recharge of groundwater. Sinks or outflows may include spring flow, base flow to streams, evapotranspiration, and pumping. Defining the flow system involves determining the direction of groundwater flow and the hydrologic interaction between the different modeled units.

(c) Define the transport system and sources and sinks of chemicals in the system. The conceptual model has to include a representation of the time variant chemical source concentration, mass or volume of spill, and the chemical and biological processes affecting those chemicals.

Step 3: Select the governing equation and a computer code. Both the governing equation and code should be verified. Verification of the governing equation demonstrates that it describes the physical, chemical and biological processes occurring. Code verification can be accomplished by comparing the model results to an analytical solution of a known problem.

Step 4: Design the model. This step includes selection of a grid design, time parameters, initial and boundary conditions, and developing estimates of model parameters.

Step 5: Calibrate the design model. Calibration refers to the process of determining a set of model input parameters that approximates field measured heads, flow and/or concentrations. The purpose of calibration is to establish that the model can reproduce field-measured values of the unknown variable. It is noted that calibration is quite subjective and in many cases does not yield a unique set of parameters that reproduce field conditions.

Step 6: Determine the effect of uncertainty on model results. This is sometimes referred to as a sensitivity analysis. This is done by varying the model parameters individually within a range of possible values and noting down the results.

Step 7: Verify designed and calibrated model. This step involves testing the models ability to reproduce another set of field measurements using the model parameters that developed in the calibration process.

Step 8: Predict results based on calibrated model.

Step 9: Determine the effects of uncertainty on the model prediction.

Step 10: Present modeling design and results.

Step 11: Post audit and redesign the model as necessary.

4.4 TYPES OF ERROR

There are two main types of error.

4.4.1 Computational Error

They occur because of numerical approximation procedures that are used to solve the governing equations. They are estimated by applying continuity equation or the principle of conservation of mass.

4.4.2 Calibration Error

They occur due to model assumptions and limitations in parameter estimation. These errors can be quantified by comparing the model's predicted values to observe of the unknown variable.

4.5 DRAWBACKS AND USEFULNESS OF THE MODELING

The main complaint of models is that they require great quantities of data and are therefore too expensive to assemble and run. Furthermore, models can never be proven to be correct. On the other hand, some argue that models are essential for performing complex analysis and for making informed decisions. Models allow more effective use of the available data; the implications of proposed courses of action at the field scale can be analyzed and evaluated with them.

4.6 APPLYING NUMERICAL MODELS TO FIELD SITES

Good field data are essential when using a model for simulating existing flow and/or contaminant conditions at a site or when using a model for predictive purposes. However, an attempt to model a system with insufficient data may be useful because it may serve as a method for identifying those areas where detailed field information needs to be collected.

CHAPTER 5

PROCESSING MODFLOW FOR WINDOWS (PMWIN)

5.1 INTRODUCTION

Processing Modflow was originally developed for a remediation project of a disposal site in the coastal region of North Germany. It was designed as a pre and postprocessor for the groundwater flow model MODFLOW. PMWIN offer a totally integrated simulation system for modeling groundwater flow and transport processes with MODFLOW-88, MODFLOW-96, PMPATH, MT3D, MT3DMS, MOC3D, PEST and UCODE. It comes complete with a professional graphical pre and postprocessor.

5.2 PACKAGES UNDER PMWIN

A brief summary of the various packages under PMWIN is given below:

5.2.1 MODFLOW

MODFLOW (*McDonald and Harbaugh, 1988*) supports the simulation of the effects of wells, rivers, reservoirs, drains, head-dependent boundaries, time-dependent fixed-head boundaries, cut-off walls, compaction and subsidence, recharge and evapotranspiration. In addition to these standard packages of MODFLOW-96, PMWIN includes the unique Density package for taking into account the density driven flow rates into flow models.

5.2.2 PMPATH

The PMPATH (*Chiang and Kinzelbach, 1994, 1998*) uses a semi-analytical particle tracking scheme to calculates and animates the particle tracking processes simultaneously and provides various on-screen graphical options including head contours, drawdown contours and velocity vectors. Both forward and backward particle-tracking schemes are allowed for steady state and transient flow fields.

5.2.3 MT3D

The MT3D (*Zheng, 1990*) uses a mixed Eulerian-Lagrangian approach to simulate changes in concentration of single species miscible contaminants in groundwater considering advection, dispersion and simple chemical reaction. The chemical reactions included in the model are limited to equilibrium controlled linear or non-linear sorption and first-order irreversible decay or biodegradation.

5.2.4 MT3DMS

The MT3DMS (*Zheng and Wang, 1998*) is a further development of MT3D. The abbreviation MS denotes the Multi- Species structure for accommodating add-on reaction packages. MT3DMS includes three major classes of transport solution techniques, i.e., the standard finite difference method; the particle tracking based Eulerian-Lagrangian methods; and the higher-order finite-volume TVD method. Up to 30 different species can be simulated with PMWIN.

5.2.5 MOC3D

The MOC3D (*Konikow, Goode and Homberger, 1996*) transport model uses the method of characteristics to compute changes in concentration of a single dissolved chemical constituent over time that are caused by advective transport, hydrodynamic dispersion (including both mechanical dispersion and diffusion), mixing or dilution from fluid sources, and mathematically simple chemical reactions, including decay and linear sorption represented by a retardation factor.

5.2.6 PEST and UCODE

The PEST (*Doherty, Brebber and Whyte, 1994*) and UCODE (*Poeter and Hill, 1998*) assist in data interpretation and in model calibration. If there are field or laboratory measurements, PEST and UCODE can adjust model parameters and/or excitation data in order that the discrepancies between the pertinent model-generated numbers and the corresponding measurements are reduced to a minimum. The following model parameters can be automatically calibrated: (1) horizontal hydraulic conductivity or transmissivity; (2) vertical leakance; (3) specific yield or confined storage coefficient; (4) pumping rate of wells; (5) conductance of drain, river, stream or head-dependent cells; (6) recharge flux; (7) maximum evapotranspiration rate; and (8) inelastic storage factor.

5.3 MODFLOW

MODFLOW, a modular three-dimensional finite difference groundwater flow model developed by the U. S. Geological Survey simulates saturated flow in three dimensions. MODFLOW is probably the most widely used, tested and verified model today because of its versatility and an open structure.

The "original" version of MODFLOW-88 was developed by Michael G. McDonald and Arlen W. Harbaugh in 1988. MODFLOW-88 and MODFLOW-96 can simulate the effects of wells, rivers, drains, head-dependent boundaries, recharge and evapotranspiration. Since the publication of MODFLOW numerous investigators have developed various codes. These codes are called packages, models or sometimes simply programs. Packages are integrated with MODFLOW, each package deals with a specific feature of the hydrologic system to be simulated, such as wells, recharge or river. Models or programs can be stand-alone codes or can be integrated with MODFLOW. A standalone model or program communicates with MODFLOW through data files. The advective transport model PMPATH, the solute transport model MT3D, MT3DMS and the parameter estimation programs PEST and UCODE use this approach. The solute transport model MOC3D is integrated with MODFLOW. This code uses MODFLOW as a function for calculating flow fields.

MODFLOW is coded in FORTRAN and requires a specific data input format. The major inputs required for running MODFLOW are:

- Model grid size and aquifer's thickness
- Horizontal and vertical hydraulic conductivity of the soil of the model area
- Recharge to aquifers (area and point source)

- Ground water boundary conditions

Boundary conditions for the modeled area could be established with a prior knowledge of the area. The types of boundary conditions MODFLOW uses are:

- Constant head boundary, e.g., a river or a reservoir
- No flow boundary, e.g., an impermeable layer such as mountain bedrock
- Constant flux, e.g., a constant flux of water, such as a stream inlet or ground water recharge from neighboring aquifers.

The major outputs from MODFLOW are the predicted ground water elevation or head for each grid cell in the model along with a water budget (mass balance) for each grid cell. These two outputs can be used as inputs to run MT3D.

A step-by-step explanation of the various parameters under MODFLOW package is given below:

5.3.1 Grid

MODFLOW uses the block-centered grid (Fig. 5.1) in which the model calculates the head at the center of each cell i.e. the node. It is assumed that hydraulic and hydrogeologic properties are uniform over the extent of a cell so that the cell is represented by the node.

In MODFLOW the origin of the grid is in the upper left corner of the grid and the layers are numbered from top down. An aquifer system is discretized into a mesh of blocks, or cells, the locations of which are described in terms of rows (I), columns (J), and layers (K) as illustrated in Fig. 5.2.

The grid mesh can be uniform, when all the cells have same dimensions, and custom, when cell sizes varies. Although the uniform grid is preferred from a mathematical standpoint, it will often be necessary to design a custom grid. A rule of thumb when designing a custom grid is that the size of a cell, in all three directions (row, column, layer), cannot be more than 1.5 times larger (smaller) than the size of the adjacent cells. This is necessary in order to preserve the mathematical stability of the numerical solution.

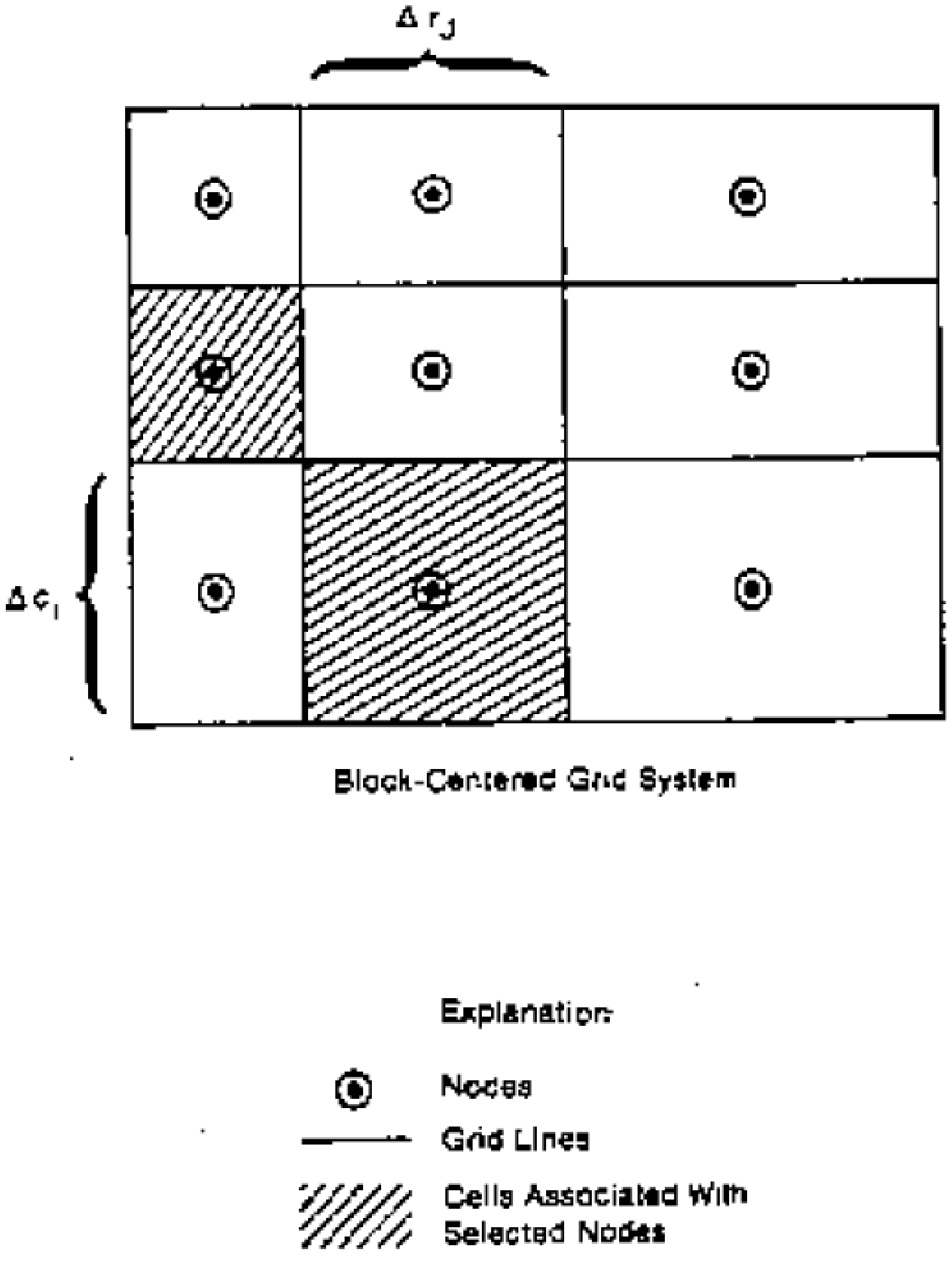
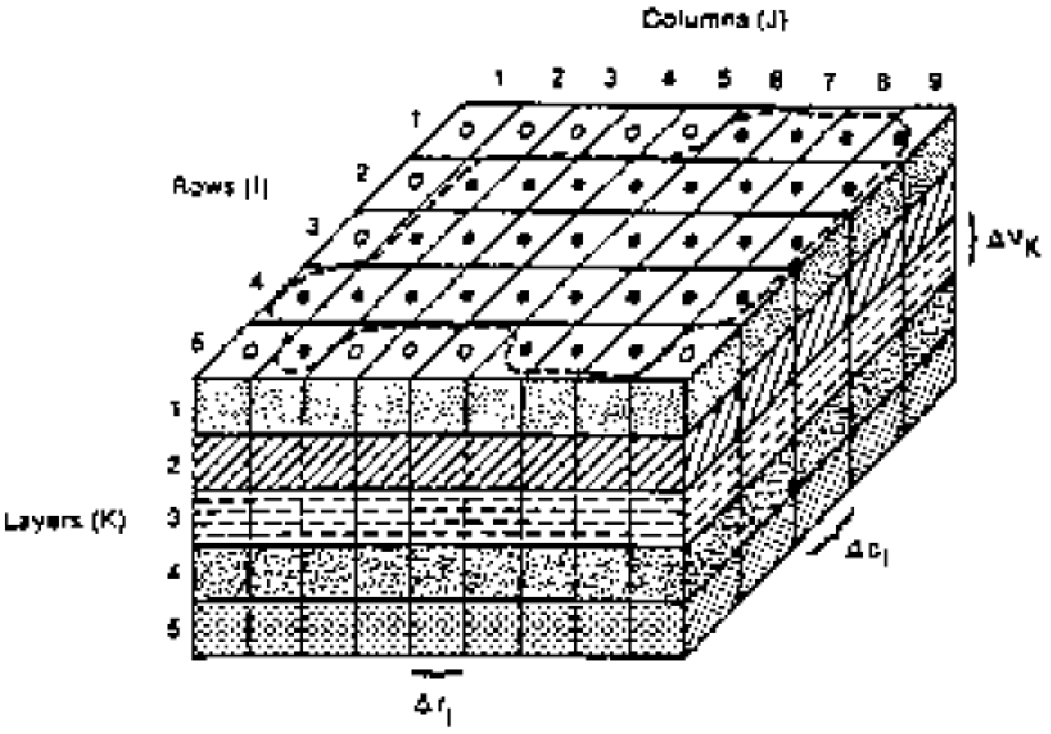


Fig. 5.1 Diagram showing Block Centered Grid System (*after McDonald and Harbaugh, 1988*)



- - - - - Aquifer Boundary

• Active Cell

o Inactive Cell

Δr_j Dimension of cell along the row direction. Subscript (j) indicates the number of the column

Δc_i Dimension of cell along the column direction. Subscript (i) indicates the number of the row

Δv_k Dimension of cell along the vertical direction. Subscript (k) indicates the number of the layer

Fig. 5.2 Spacial discretization of an aquifer system (*after McDonald and Harbaugh, 1988*)

5.3.2 Layer Type

There are four basic types of layers in MODFLOW:

- **Type 0:** This layer type is used to simulate confined conditions (layers / aquifers) in which transmissivity of each cell remains constant for the entire simulation time. For transient simulations this layer type requires the confined storage coefficient, which is used to calculate the rate of change in storage.

- **Type 1:** This layer type is used strictly for unconfined conditions and is valid for the first (uppermost) layer only. It requires specific yield for transient conditions. Transmissivity of the layer varies as saturated thickness of the aquifer changes during simulation.

- **Type 2:** This layer type is used when the aquifer alternates between confined and unconfined. However, it is assumed that the saturated thickness remains everywhere a high fraction of the layer thickness so that recalculation of transmissivity is not necessary. In transient simulations it is needed to specify both the storage coefficient for fully saturated confined conditions, and the specific yield for unconfined flow. If the layer completely desaturates, vertical leakage from above ceases.

- **Type 3:** This layer type is also used for confined unconfined transitions. It includes varying transmissivity, which is recalculated at each iteration using hydraulic conductivity and new saturated thickness. Confined storage coefficent and specific yield are both needed for transient simulations. Vertical leakage from above terminates when the layer is completely dry.

5.3.3 Boundary Condition

(1) IBOUND (MODFLOW)

An IBOUND array is required by the flow model MODFLOW. Three types of boundary conditions are possible in IBOUND

- An active cell denoted by 1, in which the hydraulic head is calculated by the model and are free to vary with time.

- A fixed-head cell denoted by -1, in which the hydraulic head is kept fixed at a given value such as aquifer contacts with major surface water features.
- An inactive cell denoted by 0, in which no flow into or out of the cell occurs during the entire time of simulation.

(2) ICBUND (MT3D)

An ICBUND array is required by the transport models MT3D and MT3DMS.

- An active concentration cell denoted by 1, in which the concentration varies with time and is calculated by the model.
- A constant concentration cell denoted by -1, in which the concentration is constant.
- An inactive concentration cell denoted by 0, in which no transport simulation takes place at such cells.

5.3.4 Layer Top and Bottom

The elevation of the layer top and bottom is required to calculate aquifer transmissivity, vertical leakance or confined storage coefficient. Original MODFLOW reads the top elevation only for layers of type 2 and 3, and the bottom elevation for layers of type 1or 3.

5.3.5 Time

Time parameters are specified when modeling transient (time dependent) conditions. They include time unit, the length and number of time periods, and the number of time steps. During one time (stress) period all model parameters associated with boundary conditions and various stresses remain constant. A time period is further divided into time steps that are useful for analyzing changes in hydraulic head and drawdown. Time steps do not have to be of same length.

5.3.6 Initial Hydraulic Heads

MODFLOW requires initial hydraulic heads at the beginning of a flow simulation. For transient flow simulations, the initial heads must be the actual values.

For steady-state flow simulations, the initial heads are starting guessed values for the iterative equation solvers. The heads at the fixed-head cells must be the actual values while all other initial heads can be set arbitrarily.

5.3.7 Horizontal Hydraulic Conductivity and Transmissivity

In MODFLOW the horizontal hydraulic conductivity is the conductivity along the grid rows. The hydraulic conductivity is required for layers of type 1 and 3 (unconfined conditions), and transmissivity is required for layers of type 0 and 2 (confined conditions). Most MODFLOW processors like PMWIN can calculate transmissivity for a layer of any type by multiplying hydraulic conductivity with layer thickness derived from layer top and bottom elevations.

5.3.8 Vertical Hydraulic Conductivity and Leakance

For quasi-3D models with more than one layer and for full 3D models, MODFLOW requires the input of the vertical leakance between two layers. Processors such as PMWIN can calculate the vertical leakance for each layer from the layer thickness and the vertical hydraulic conductivity. Unless accurately determined from pumping tests, the vertical hydraulic conductivity is usually assumed and/or calibrated.

5.3.9 Storage Terms

Storage coefficient for confined layers (layer type 0, 2, and 3) and specific yield for unconfined layers (layer type 1, 2, 3) are required only for transient simulations. The storage coefficient (S) is the product of the layer thickness (b) and specific storage (S_s)

$$S = b.S_s \tag{5.3.1}$$

5.3.10 Effective Porosity

The volume percentage of a rock or soil sample that consists of interconnected pores through which water can flow is the effective porosity. It is used by transport models, for example PMPATH, MOC3D, MT3D to calculate the average velocity of the flow through the porous medium.

5.3.11 MODFLOW Packages

(1) Density Package

In the Density Package developed by Schaars and Van Gerven (1997), the water density of a "density-layer" may differ from cell for cell. During a flow simulation the density-dependent flows will be adapted into the system of flow equations by correcting the hydraulic heads to equivalent fresh water heads (or reference density heads).

(2) Drain Package

The Drain Package simulates both closed and open drains. It is one of the best tools to model springs since the inflow into the drain ceases when the head in the aquifer drops below drain elevation.

(3) Evapotranspiration Package

The Evapotranspiration Package simulates the effects of plant transpiration and direct evaporation in removing water from the saturated groundwater regime. This package shows a linear variation in the water table elevation accounting for the user specified maximum and minimum (zero) depth of evapotranspiration.

(4) General Head Boundary Package

The General Head Boundary Package is used for transient simulations of constant head boundaries since it allows the user to change the head from one time period to another. It can be used to simulate permanent surface water features.

(5) Horizontal Flow Barrier Package

The Horizontal-Flow Barrier Package developed by Hsieh and Freckleton (1993), simulates thin low-permeability geologic features, such as vertical faults or slurry walls that impede the horizontal flow of groundwater. These geologic features are approximated as a series of horizontal-flow barriers conceptually situated on the boundaries between pairs of adjacent cells in the finite-difference grid.

(6) Interbed Storage Package

The Interbed Storage Package developed by Leake and Prudic (1991), calculates the water volume released from storage and simulates elastic and inelastic compaction of compressible fine-grained beds in an aquifer due to groundwater extraction. The term “interbed” is used to denote a poorly permeable bed within a relatively permeable aquifer. This package is used only for transient simulations.

(7) Recharge Package

The Recharge Package is typically used to simulate areal infiltration from precipitation or irrigation. It can also simulate local recharge to ponds. It is flexible in assigning vertical flux to different layers along the vertical.

(8) Reservoir Package

The Reservoir package developed by Fenske, Leake and Prudic (1996) can simulate leakage from reservoirs where the reservoirs are much greater in area than the area represented by individual model cells. More than one reservoir can be simulated using this package.

(9) River Package

The River Package simulates the flow between an aquifer and a surface water feature in both directions. It includes riverbed conductance for simulating fine sediment clogging of a river channel. It should not be used for intermittent streams since there is no adjustment for the stream flow and stage once it drops below the channel bottom.

(10) Streamflow Routing Package

The Streamflow Routing Package developed by Prudic (1989), simulates interaction between an aquifer and a surface stream accounting for the flow rate in the stream. Flow into or out of the stream stops when the stream dries out. It requires intensive data preparation and more data input than any other package.

(11) Time-Variant Specified-Head Package

The Time-Variant Specified-Head Package developed by Leake and Prudic (1988) is used in transient simulations and allows constant head cells to take on different head values for each time step during a simulation time period.

(12) Well Package

The Well Package simulates both extraction and recharge wells. Negative cell values for the "Rechage rate of the well" are used to indicate pumping wells, while positive cell values indicate injection wells. It assumes full penetration of the layer.

(13) Block-Centered Flow 2 Package

The Block-Centered Flow 2 Package developed by McDonald, Harbaugh, Orr and Ackerman (1992) allows the simulation of a rising water table into unsaturated (dry) model layers. A typical application is the simulation of the recovery of over stressed aquifer, such as after heavy pumpage, either through artificial recharge or the reduction of stress.

5.3.12 Model Run

After the model parameters are assigned to each cell, to run the model the user must choose one of the solving packages. PMWIN supports four packages (solvers) for solving systems of simultaneous linear equations:

- The Direct Solution (DE45) package,
- The Preconditioned Conjugate-Gradient 2 (PCG2) package,
- The Strongly Implicit Procedure (SIP) package, and
- The Slice-Successive Overrelaxation (SSOR) package.

The number of model runs during calibration will depend on the quantity and quality of available data, desirable accuracy of the model results.

5.4 MATHEMATICAL MODEL OF MODFLOW

The three-dimensional movement of groundwater of constant density through porous earth material underlying the groundwater flow model MODFLOW may be described by the partial differential equation:

$$\frac{\partial}{\partial x}\left(K_{xx}\frac{\partial h}{\partial x}\right)+\frac{\partial}{\partial y}\left(K_{yy}\frac{\partial h}{\partial y}\right)+\frac{\partial}{\partial z}\left(K_{zz}\frac{\partial h}{\partial z}\right)-W=S_s\frac{\partial h}{\partial t} \qquad (5.4.1)$$

where

K_{xx}, K_{yy}, K_{zz} are the values of hydraulic conductivity along the x, y and z coordinate axes, which are assumed to be parallel to the major axes of hydraulic conductivity [LT^{-1}];

h is the potentiometric head $[L]$;

W is the volumetric flux per unit volume and represent sources and / or sinks of water [T^{-1}]

S_s is the specific storage of the porous material [L^{-1}]

t is the time $[T]$

A solution to equation (5.4.1) in an analytical sense, is an algebraic expression giving h(x,y,z) such that, when the derivatives of h with respect to space and time are substituted in equation (5.4.1), the equation and its initial and boundary conditions are satisfied. Except for very simple systems, analytical solution of equation (5.4.1) are rarely possible, so various numerical methods must be employed to obtain approximate solutions.

MODFLOW uses one such numerical method i.e. Finite Difference Method, wherein the continuous system described by equation (5.4.1) is replaced by a finite set of discrete points in space and time and the partial derivatives are replaced by terms calculated from the differences in head values at these points. The process leads to systems of simultaneous linear algebraic difference equations; their solution yields values of head at specific points and times. These values constitute an approximation to the time varying head distribution that would be given by an analytical solution of the partial difference equation of flow.

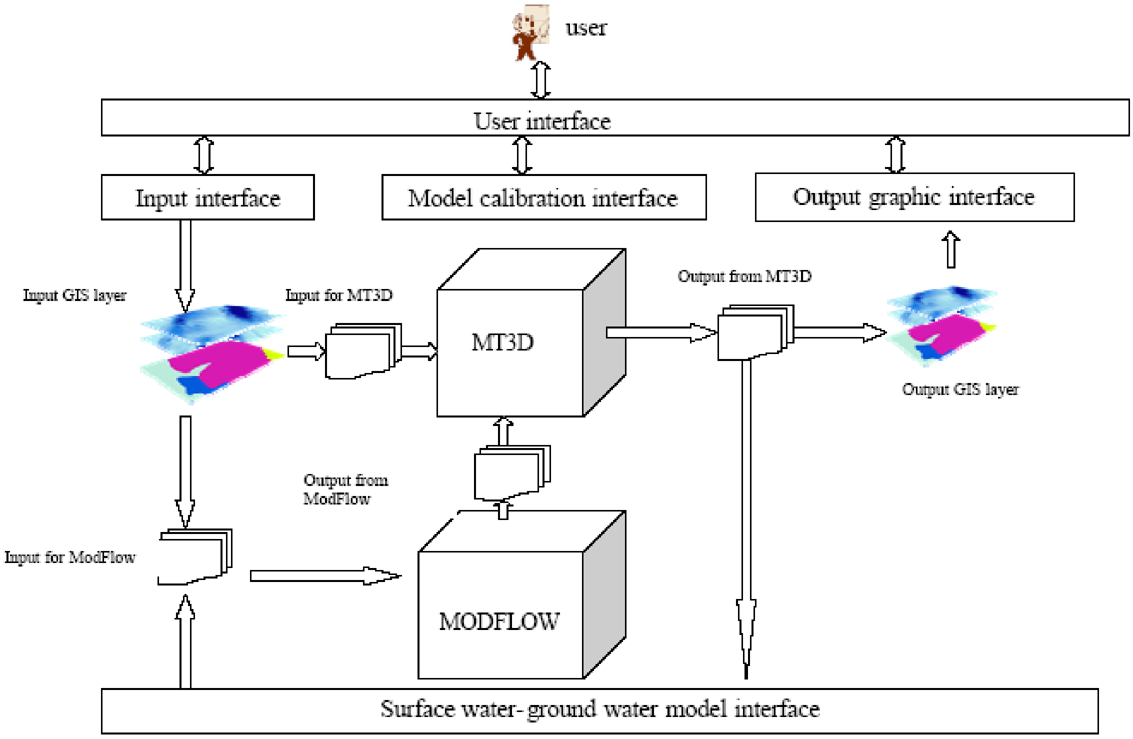


Fig. 5.3 Schematic structure of the ground water modeling component.

5.5 MT3D

MT3D, a Modular Three-Dimensional Transport Model developed by the U.S Geological Survey uses a mixed Eulerian-Lagrangian approach to the solution of the three-dimensional advective-dispersive-reactive transport equation. MT3D is based on the assumption that changes in the concentration field will not affect the flow field significantly. This allows the user to construct and calibrate a flow model independently. After a flow simulation is complete, MT3D simulates solute transport by using the calculated hydraulic heads and various flow terms saved by MODFLOW.

Currently, MT3D accommodates the following spatial discretization capabilities and transport boundary conditions:

- Confined, unconfined variably confined/unconfined aquifer layers;
- Solute transport effects of extemal sources and sinks such as wells, drains, inclined model layers and variable cell thickness within the same layer;
- Specified concentration or mass flux boundaries;
- The rivers, areal recharge and evapotranspiration.

MT3D can be used to simulate changes in concentration of single species miscible contaminants in groundwater considering advection, dispersion and some simple chemical reactions. The chemical reactions included in the model are limited to equilibrium controlled linear or non-linear sorption and first-order irreversible decay or biodegradation.

Like the MODFLOW model, the MT3D model consists of a main program and a large number of highly independent subroutines, called modules, which are grouped into a series of "packages". Each of these packages deals with a single aspect of the transport simulation.

The major input required for running MT3D are:

- Ground water head and water mass budget generated by MODFLOW,
- Model grid size and aquifers thickness,
- Hydraulic parameters (such as conductivity) of the aquifer material,
- Effective soil porosity at each model cell,
- Advection numerical solver parameters,
- Soil dispersion and diffusion effect parameter (longitudinal dispersivity, horizontal/ transverse dispersivity, vertical dispersivity and diffusion coefficient),
- Pollutant loading source location, type and rate.

The major output form MT3D is an unformatted file of pollutant concentrations for the model grid cells at a specified time.

A step-by-step explanation of the various parameters under MT3D is given below:

5.5.1 Initial Concentration

The initial concentration at each active cell is required at the beginning of a transport simulation.

5.5.2 Advection Package

The Advection Package solves the concentration change due to advection with one of the four schemes included in the package:

- Method of characteristics (MOC)
- Modified method of characteristics (MMOC)
- Hybrid method of characteristics (HMOC)
- Upstream finite difference method.

5.5.3 Dispersion Package

The Dispersion Package solves the concentration change due to dispersion with the explicit finite difference method. This package requires:

- Longitudinal dispersivity of the aquifer,
- The ratio of the horizontal transverse dispersivity to the longitudinal dispersivity
- The ratio of the vertical transverse dispersivity to the longitudinal dispersivity
- Effective molecular diffusion coefficient.

5.5.4 Chemical Reaction Package

The Chemical Reaction Package solves the concentration change due to chemical reactions. Currently, the chemical reactions include linear or nonlinear sorption isotherms and first order irreversible rate reactions (radioactive decay or biodegradation).

5.5.5 Sink & Source Concentration Package

The Sink & Source Concentration Package solves the concentration change due to fluid sink/source mixing with the explicit finite difference method. Point sources include wells, general-head boundary cells, fixed-head cells, rivers and streams. Recharge is the only areally distributed source whereas evapotranspiration is the only sink whose concentration can be specified.

5.6 MATHEMATICAL MODELING OF MT3D

The governing advective-dispersive-reactive solute transport equation in three dimensions underlying in the transport model MT3D can be describe by the partial differential equation:

$$R\frac{\partial C}{\partial t}=\frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right)-\frac{\partial}{\partial x_i}\left(v_i C\right)+\frac{q_s}{\theta}C_s-\lambda\left(C+\frac{\rho_b}{\theta}\overline{C}\right) \tag{5.6.1}$$

where

C is the concentration of contaminants dissolved in groundwater [ML^{-3}]

t is time [T]

x_i is the distance along the respective Cartesian coordinate axis [L]

D_{ij} is the hydrodynamic dispersion coefficient [L^2T^{-1}]

v_j is the seepage or linear pore water velocity [LT^{-1}]

q_s is the volumetric flux of water per unit volume of aquifer representing sources (positive) and sinks (negative) [T^{-1}]

C_s is the concentration of the sources or sinks [ML^{-3}]

θ is the porosity of the porous medium dimensionless

ρ_b is the bulk density of the porous medium [ML^{-3}]

$\overline{C}$ is the concentration of contaminants sorbed on the porous medium [MM^{-1}]

λ is the rate constant of the first-order rate reactions [T]

R is the retardation factor defined as

$$R=1+\frac{\rho_b}{\theta}\frac{\partial\overline{C}}{\partial C} \tag{5.6.2}$$

CHAPTER 6

MATERIALS AND METHODS

6.1 THE STUDY AREA

The study area, within the Yamuna Sub-basin (Fig. 6.1), covers the two districts of Nadia and N 24 Parganas in West Bengal. The study area is located between the latitudes $22^0 49^/$ and $23^0 03^/$ N and longitudes of $88^0 24^/$ and $88^0 51^/$ E and is a part of the upper Ganga Brahmaputra delta. Blocks that are studied under Nadia district are Chakdah and Haringhata, and under North 24 Parganas are Bangaon, Barackpore, Amdanga, Habra-I, Habra-II, Gaighata and Baduria. Arsenic was noted early in 1985 in these areas.

Bhagirathi river flowing north to south forms the western boundary of the study area and Ichamati river forms the eastern boundary demarcating India-Bangladesh boundary.

The Yamuna sub-basin shows a flat terrain having a master slope of 1: 25000 from northwest to southeast. The actual basin area is about 650 sq km but the study area has been chosen as 1500 km^2 with 50 km in the E-W direction and 30 km in the N-S direction.

Rural water supply of West Bengal, excepting for its smaller part of hilly region, is more or less dependent upon groundwater. About 30% of rural population is covered by piped water supply system and the rest with tube wells fitted with hand pumps. This groundwater was found to be infested with arsenic in 9 out of 18 districts stretching from Malda in north to South 24 Parganas in south.

In the study area, the main source of water is the groundwater from these tube wells, which are generally having arsenic above the permissible level of 50 μg/l. Even though the state was and still, is facing such a huge problem, the Govt. could not develop a comprehensive water quality surveillance system and a village specific arsenic contamination database due to lack of proper infrastructure, lack of laboratory facilities etc.

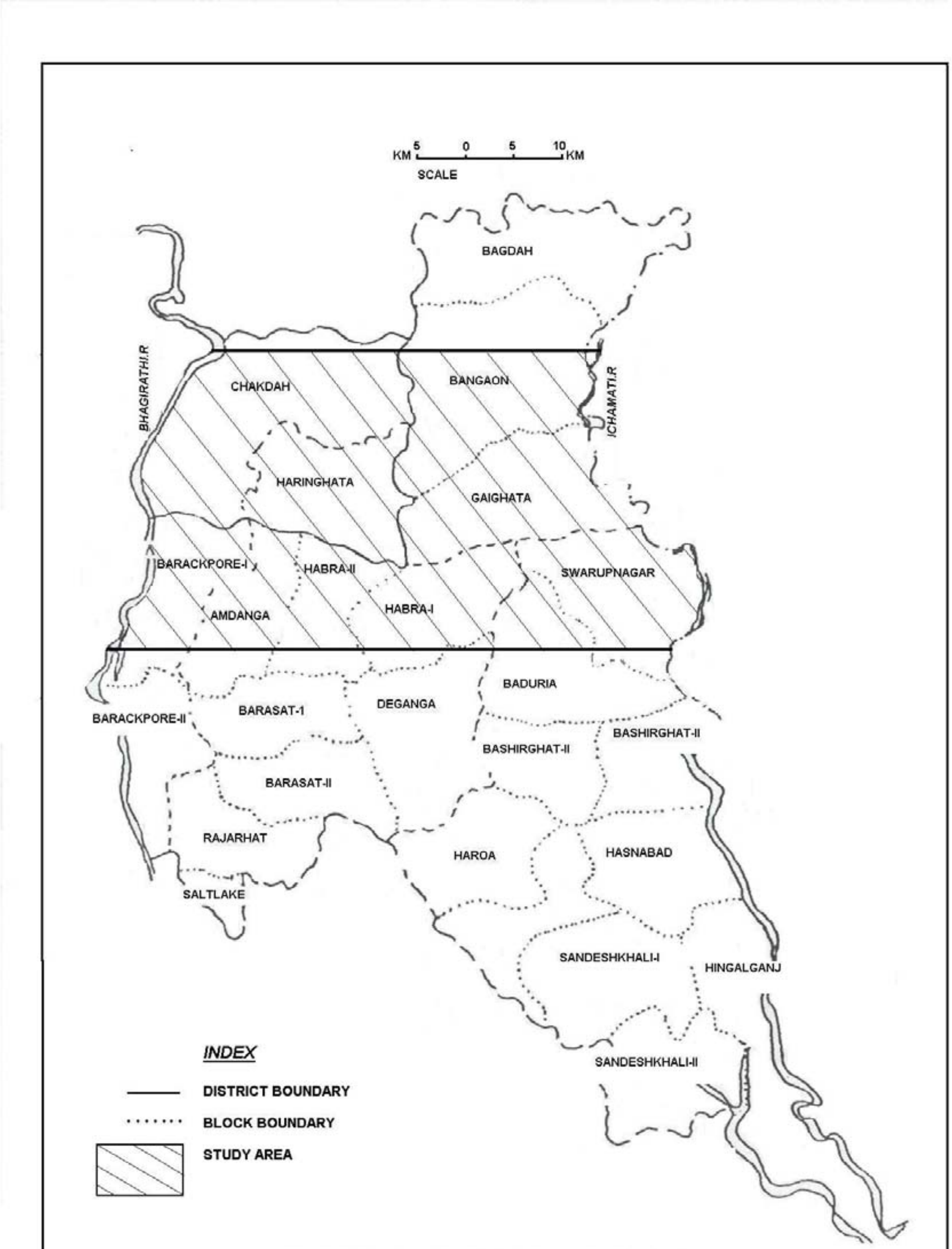


Fig. 6.1 Map showing the blocks under the study area

Another major problem for not containing the arsenic problem was the unshakable faith created over the last 50 years in the purity of tube well water. This problem of arsenic contamination has been complicated by the large variability at both the local and regional scale.

6.2 HYDROLOGY OF THE STUDY AREA

The hydrology of the study area will be discussed in two parts i.e. the surface water hydrology and the groundwater hydrology.

6.2.1 Surface Water Hydrology

The study area has a hot and humid climate, which may be due to its proximity to the Bay of Bengal. It receives a rainfall of about 1850 mm/year mostly from the SW monsoon, which occur during the months from May to September. June and July shows the maximum recorded rainfall with the area receiving about 80% of the total rainfall. For simplicity of the model, only one stress period is assumed and hence a uniform rainfall of 1850mm /year is taken.

The study area has an evaporation rate of about 50-60 mm/yr and evapotranspiration rate of about 100-110mm/yr. The two main sources of groundwater recharge in the study area are rainfall and irrigation return flows from the agricultural lands. The groundwater recharge data for the area was not available and hence was assumed as 4.5% of the total rainfall. Even though the soil is alluvial and a high recharge rate is expected, a lower value is assumed because of the fact that the depth of soil available for recharge is very less. This is due to the high depth to water table, which is of the range between 2.5-3.0m (pre-monsoon) and 0.5-2.5m (post-monsoon) below ground level.

Ichamati river has an yearly average water level of 5.5m (above MSL) with the maximum monsoon water level of 7.5m (above MSL) and minimum water level of 3.5m (above the MSL). The water level of Bhagirathi river was not accessible and is assumed to be 6.0 m (above MSL). The Bhagirathi river had a bed slope of

1:15,000 and cross-sectional average velocities of 0.5m/s in November 1998. The same values for Ichamati river were 1:20,000 and 0.3m/s respectively.

6.2.2 Groundwater Hydrology

The groundwater in the study area is reported to occur under unconfined to semi-confined condition. It has also been reported that the top 20-30 meters are local clay and sandy clay layers. According to an unpublished assessment report by Central ground Water Board, Kolkatta (1991), there are about 29,058 shallow tube wells and 197 heavy-duty tube wells in the study area. The shallow tube wells, having tapping zones in between 18-50mbgl, are mainly use for irrigation purposes and have a discharge rate between 23-43 m^3/h. The deep tube wells, having tapping zones in between 60-150mbgl, are mainly use for domestic and municipal supplies and have a discharge rate between 45-200 m^3/h.

6.3 LITHO LOGS AND ARSENIC LEVELS OF THE STUDY AREA

Thirty-two litho logs were prepared by the Central Ground Water Board (CCWB), West Bengal for the study area. The maximum depth of available logs is of 400.21m at Adarshapally (Khardah), while the minimum one goes only 25m deep at Rudrapur (Block: Baduria). None of these logs, however, reach the basement rock. The thickness of each lithological unit changes abruptly and there is no distinct aquifer - aquitard system. Because of the unavailability of elevation data for all of the locations from the mean sea level, all of them have been considered to be at the same level of 7.5m above MSL.

These litho logs were simplified by broadly grouping the various lithological layers as Clay group, Sand group, Sand and Gravel. The numbering of the different litho logs is done from bottom to top to facilitate easy understanding of the litho logs. These thirty-two simplified litho logs were further simplified to get a litho log for the entire Yamuna sub basin. This was done by taking the average of the similar lithological layers for the whole study area. The simplified litho log for the entire sub basin is given in Table 6.1. Since the litho log data below 140m was less, only a generalized picture upto 140m is given here.

The resulting litho log is a three-tier multi-aquifer-aquitard with Sand and Gravel as the lowest aquifer and Sand as the next two aquifers. All these aquifers are separated by clay aquitards. These six hydro-stratigraphic units are of variable thickness, but for modeling purpose the thickness of different units are taken as that of the simplified litho log for the Yamuna sub-basin. All the aquifers are confined, though locally they may be semi-confined due to the presence sandy clay in the clay group.

Unit	Lithology	Depth (m)	Thickness (m)
6.	Clay Group	0-25	25
5.	Sand	25-42	17
4.	Clay Group	42-70	28
3.	Sand	70-90	20
2.	Clay Group	90-100	10
1.	Sand and Gravel	100-140	40

(After Mukherjee 2004)

Table 6.1 Simplified litho-log for the Yamuna Sub basin, West Bengal

The hydraulic parameters of the aquifer material were not available, nor were the size range of the soil grain at different depths. This data unavailability forced the author to assume the hydraulic conductivities and effective porosity values for the different lithologies from some reliable sources.

In Chakdaha and Haringhata blocks of Nadia District, the arsenic concentration in groundwater range from 0.05 to 0.07 ppm and in Amdanga, Baduria, Barackpore-I, Bangaon, Gaighata, Swarupnagar, Habra-I and Habra-II blocks of N 24 Parganas District, the range was between 0.05 -1.18ppm.

6.4 GROUNDWATER FLOW MODELING USING MODFLOW & SOLUTE TRANSPORT MODELING USING MT3D

The groundwater quantity-modeling component used here is MODFLOW and the pollutant transport component is MT3D. MODFLOW and MT3D, used in this study, is part of the software Processing Modflow for Windows (PMWIN). The combined hydrologic and water quality model requires the compilation of considerable data sources to accurately capture the dynamical processes prevalent within the hydrologic systems. Unfortunately the data available for the model domain was not sufficient and some aquifer properties had to be assumed. These assumptions might have created some unavoidable discrepancies in the results.

The first part of the modeling involves developing a groundwater model to adequately simulate a steady-state flow in the aquifer using MODFLOW.

The three-dimensional model domain is a 50 km by 30 km area situated in the Yamuna Sub-basin which is discretized into grids of 2000m $\times$2000m. As the maximum limit of nodes of grid possible in this educational issue of PMWIN is only 4000, a two-layer system, instead of the actual six-layer system, consisting of the topmost layers is assumed. After a distance of 8000m each from the western and northern end of the model, the size of the grids were decreased by a factor of 1.5 so as to get a well of 10m $\times$ 10 m, where the arsenic is to be injected for MT3D simulation. This is done in accordance with a rule of thumb, which says that when designing a custom grid the size of a cell, in all three directions (row, column, layer), cannot be more than 1.5 times larger (smaller) than the size of the adjacent cells. This is necessary in order to preserve the mathematical stability of the numerical solution. The custom grid is shown in Fig. 6.2.

The model has 36 rows, 46 columns and 2 layers, the first layer having a depth of 25m and the second layer of 17m. These values are obtained from the simplified litho logs of the sub basin. The top layer of the model is the clay group and the second layer is the sand group. The clay layer is assumed to be semi-confined and the sand layer to be confined. The Hydraulic parameters of these two layers are given in Table

6.2. The flow was to be simulated over a period of 20 years for every 1 year. A stress period of 20years was assumed for the simulation.

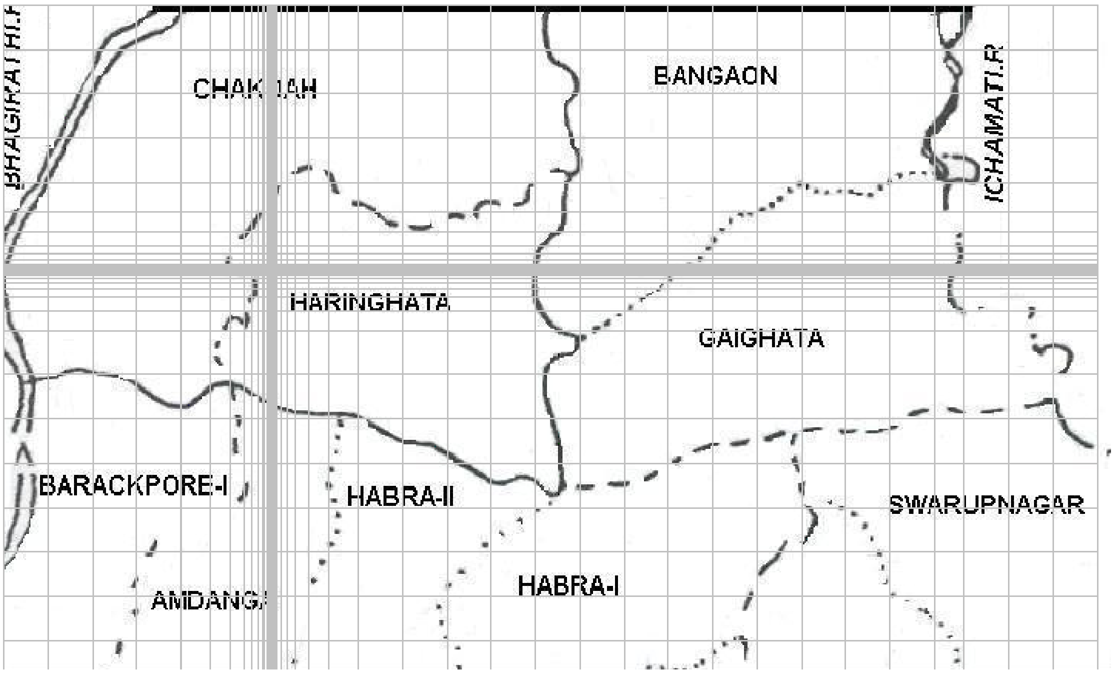


Fig. 6.2 Custom grid of the model.

Constant-head boundaries were applied to the Bharirathi and Ichamati rivers forming the western and eastern boundary of the model domain. The other cells were provided with variable head boundaries. The constant hydraulic head of Ichamati river is 5.5 m above MSL and that of the Bhagirathi river is assumed to be 6.0m above MSL. The recharge rate of the study area was assumed as 4.5% of the total rainfall.

The model domain has about 29058 shallow tube wells having discharge rate between 23- 43 m^3/h and 197 heavy-duty tube wells having discharge rate between 45 - 200 m^3/h. Such a huge number of extraction tube wells could be shown on the model because of the limited number of cells and unavailabity of exact locations of the wells. To solve this problem, a uniform distribution of wells in the whole model domain was assumed. The average discharge rate of the shallow tube wells and the heavy-duty tube wells were assumed to be 30 m^3/h and 100 m^3/h respectively. The average extraction of water from the aquifer per unit area was now calculated as

$1.651\times10^{-7} m^3/s/m^2$. Almost all the pumping of water is assumed to be from the sand aquifer with the clay aquitard giving negligible contribution. Thus a negligible pumping rate of $1\times10^{-12} m^3/s/m^2$ is assumed for the clay layer. The MODFLOW package was run and the simulated hydraulic heads for the 2 layers was obtained in the form of contour maps.

Sl.No.	**Parameters**	**Unit**	**Values**
1.	Horizontal Hydraulic Conductivity for Clay	m/s	4.63×10^{-9}
2.	Horizontal Hydraulic Conductivity for Sand	m/s	4.74×10^{-4}
3.	Vertical Hydraulic Conductivity for Clay	m/s	4.63×10^{-10}
4.	Vertical Hydraulic Conductivity for Sand	m/s	4.74×10^{-5}
5.	Effective Porosity	-	0.25
6.	Evapotranspiration Rate	m/s	3.171×10^{-9}
7.	Elevation of Evapotranspiration Surface	m	42.0
8.	Evapotranspiration Extinction Depth	m	38.0
9.	Recharge as % of Precipitation	%	4.5
10.	Recharge Rate	m/s	2.64×10^{-9}
11.	Pumping Rate of Well for 1st layer	$m^3/s/m^2$	-1.0×10^{-12}
12.	Pumping Rate of Well for 2nd layer	$m^3/s/m^2$	-1.651×10^{-7}
13.	Longitudinal Dispersivity for Clay	m	1.0
14.	Longitudinal Dispersivity for Sand	m	10.0
15.	$\frac{Horizontal\ Transverse\ Dispersivity}{Longitudinal\ Dispersivity}$	-	0.1
16.	$\frac{Vertical\ Transverse\ Dispersivity}{Longitudinal\ Dispersivity}$	-	0.1

Table 6.2 Parameters used for simulation of MODFLOW and MT3D.

The second part of the modeling involves the three-dimensional transport of solute injected continuously from a point source in a steady state uniform flow field. The assumptions made in this part are:
1) arsenic is injected continuously from the point source;
2) the ambient groundwater velocity is negligible relative to the velocity created by the injection;
3) the aquifer is homogeneous, isotropic, and infinite in areal extent; and
4) the flow field is steady-state.

Appendix-I gives the concentration of arsenic in groundwater at various depths of the some blocks in the Yamuna sub-basin. These datas were prepared by the Central Ground Water Board, Kolkatta. Since data for only selected depth could be obtain, it is assumed that there is no vertical variation in the concentration of arsenic. A simplified table recording the blocks under the study domain with the respective average arsenic concentration is given in Table 6.3. These are taken as the initial concentration for each block. It is further assumed that the solute concentration varies with time (active concentration cell).

Sl.No.	**District**	**Block**	**As ($\mu g/m^3$)**
1.	Nadia	Chakdah	60000
2.		Haringhata	38500
3.	N 24 Parganas	Habra I	35000
4.		Habra II	615000
5.		Baduria	205000
6.		Amdanga	75000
7.		Barackpore	60000
8.		Bangaon	145000
9.		Gaighata	145000
10.		Swarupnagar	70000

Table 6.3 Initial concentration of arsenic in different blocks within Yamuna Sub-basin.

Arsenic concentrations for a few blocks were not available in the CGWB report and were assumed. These blocks whose arsenic concentration was not available in the CGWB report were Barackpore and Bangaon blocks both in N 24 Parganas. To record arsenic concentration in the study area, 6 boreholes were assumed to be drilled. The locations of these boreholes are given in Table 6.4.

Borehole No.	Cell	Distance in the X-direction	Distance in Y-direction
1	(4,3)	8000	6000
2	(34,3)	26000	6000
3	(17,17)	12005	12005
4	(34,17)	26000	12005
5	(4,32)	8000	22000
6	(42,32)	42000	22000

Table 6.4 Location of boreholes in the study area.

100ppm/m^3 of arsenic was assumed to be injected in a well 12005m away from both the western and northern side of Yamuna Sub-basin in the block of Chakdah, Nadia district and at a depth of 25m from the ground level i.e. the (17,17,2) cell, to simulate the movement of arsenic in the aquifer. For a recharge rate of 2.64×10^9 m^3/m^2/s and concentration associated 1×10^8 µg/m^3, the dissolution rate of arsenic in the groundwater works out as 0.264µg/s/m^2.

The MODFLOW solves for the distribution of hydraulic head within the model domain and, from these results, the velocity components of flow are calculated. MT3D uses the velocity values as inputs to solve the transport equation. The transport advection term is solved by particle tracking (Lagrangian approach) and the dispersion term is solved using a finite-difference method (Eulerian approach). The assumed values of the effective porosity and longitudinal, horizontal and vertical dispersivities are given in Table 6.2. Horizontal and vertical transverse dispersivity are assumed to be one-tenth the longitudinal dispersivity . The time step is taken as 1 year.

CHAPTER 7

RESULTS AND DISCUSSION

The model used, Processing Modflow for Windows (PMWIN), offers a totally integrated simulation system for modeling groundwater flow and transport .The program MODFLOW simulated three-dimensional groundwater flow and revealed the variation of hydraulic heads in the study area. MT3D, a modular 3D solute transport model for MODFLOW for simulation of advection, dispersion and chemical reaction, simulated the movement of arsenic and revealed the impact of injection of 100ppm/m^3 of arsenic continuously in the study area. The results were compiled in the form of contour maps showing the spatial distribution of hydraulic head and arsenic concentration for different durations.

7.1 VARIATION OF HYDRAULIC HEADS

MODFLOW was used to simulate the groundwater flow in the study area. The resultant contour maps depicting the variation of hydraulic head in both the clay and sand layers are enclosed in this dissertation.

7.1.1 Variation of Hydraulic Heads in the Clay Layer (1st Layer)

Fig. 7.1 illustrates the variation of hydraulic heads in the clay layer of the study area. Table 7.1 gives the values of the hydraulic heads in the clay layer at every cell 4 kms apart. The hydraulic head shows a large variation near the river i.e. the value of hydraulic gradient is high near the river and the variation becomes less towards the middle, only to increase again, thus giving a concave look.

This high hydraulic gradient near the river may be due to more relative recharge from the river at places near to it. But the aquifer material being clay, which has a low hydraulic conductivity, could not distribute the recharge uniformly. This may be the reason why a sharp concave contour is formed.

7.1.2 Variation of Hydraulic Heads in the Sand Layer (2nd Layer)

Fig. 7.2 illustrates the variation of hydraulic heads in the sand layer of the study area. Table 7.2 gives the values of the hydraulic heads in the sand layer at every cell 4 kms apart. The hydraulic head shows a gradual variation in the whole of the study area giving a smooth concave look i.e. the hydraulic gradient is almost uniform for the whole area.

This almost uniform hydraulic gradient may be due to the reason that the recharge from the river is distributed uniformly by the sand aquifer material of the study area.

7.2 DISTRIBUTION OF ARSENIC IN THE STUDY AREA

100 ppm/m^3 of arsenic was assumed to be injected continously in a well 12005m away from both the western and northern side of the study area in the block of Chakdah and at a depth of 25m from the ground level i.e. the (17,17,2) cell, to simulate the movement of arsenic in the aquifer. Simulations were performed for every 1 year for a period of 20 years to see the impact of the injected arsenic. The resultant contour maps depicting the distribution of arsenic in the study area for 1, 5, 10, 15 and 20 years are enclosed in this dissertation.

7.2.1 Distribution of Arsenic in the Clay Layer (1st Layer)

Fig. 7.3 illustrates the distribution of arsenic in the clay layer of the study area after 1 year of injection of arsenic. Fig. 7.5 illustrates the distribution of arsenic in the clay layer of the study area after 5 years of its injection. Fig. 7.7 illustrates the distribution of arsenic in the clay layer of the study area after 10 years of its injection. Fig. 7.9 illustrates the distribution of arsenic in the clay layer of the study area after 15 years of its injection. Fig. 7.11 illustrates the distribution of arsenic in the clay layer of the study area after 20 years of its injection.

Table 7.3 gives the concentration of arsenic in the clay layer of the study area after 1 year of injection of arsenic, at every cell 4 kms apart. Table 7.5 gives the concentration of arsenic in the clay layer of the study area after 5 years of injection of arsenic, at every cell 4 kms apart. Table 7.7 gives the concentration of arsenic in the clay layer of the study area after 10 years of injection of arsenic, at every cell 4 kms apart. Table 7.9 gives the concentration of arsenic in the clay layer of the study area after 15 years of injection of arsenic, at every cell 4 kms apart. Table 7.11 gives the concentration of arsenic in the clay layer of the study area after 20 years of injection of arsenic, at every cell 4 kms apart.

Fig. 7.13 compares the variation in the concentration of arsenic in the two layers in the 1st borehole. Fig. 7.14 compares the variation in the concentration of arsenic in the two layers in the 2nd borehole. Fig. 7.15 compares the variation in the concentration of arsenic in the two layers in the 3rd borehole. Fig. 7.16 compares the variation in the concentration of arsenic in the two layers in the 4th borehole. Fig. 7.17 compares the variation in the concentration of arsenic in the two layers in the 5th borehole. Fig. 7.18 compares the variation in the concentration of arsenic in the two layers in the 6th borehole.

There is a spatial and temporal variation in the concentration of arsenic due to its injection at a point in the study area. The concentration of arsenic in the study area shows an increasing trend, which shows that arsenic is spreading over the whole of the study area. The arsenic concentration after 20 years of injection had the maximum value as compared to the values after 1, 5, 10 and 15 years. Thus it can be deduced that the arsenic crisis may aggravate, affecting more and more area with the passage of time, the areas adjoining West Bengal and Bangladesh being the most susceptible.

The arsenic concentrations in the clay layer were higher than the arsenic concentrations in the sand layer at almost all nodes. But the arsenic concentrations of the sand layer in the periphery of the study area were more than that of the clay layer. This shows that arsenic moves faster in the sand layer, which may be the reason why a larger concentration of arsenic is seen in the periphery of the study area. This may be due to the larger longituidinal dispersivity value of the sand layer. Thus it can be deduced that sand layer distributes the injected arsenic at a higher rate and more uniformly. Thus neighbouring places of West Bengal and Bangladesh having sandy soil will be more susceptible to arsenic pollution than places having clayey soil.

It was seen that Habra-II, southern part of Haringhata and western side of Habra-I has the maximum concentration of arsenic, followed by Baduria, Bangaon, Gaighata, Swarupnagar, Amdanga, Chakdah and Barackpore. Even though both Habra-I and Haringhata had a low initial arsenic concentration, because of the influx of arsenic from the neighbouring block of Habra-II, western side of Habra-I and the southern side of Haringhata was seen to have maximum arsenic concentration.

The most arsenic pollution prone area in the whole of the study area is Habra-II, thus needing extra attention from the Government and other agencies.

7.2.2 Distribution of Arsenic in the Sand Layer (2nd Layer)

Fig.7.4 illustrates the distribution of arsenic in the sand layer of the study area after 1 year of its injection. Fig. 7.6 illustrates the distribution of arsenic in the sand layer of the study area after 5 years of its injection. Fig. 7.8 illustrates the distribution of arsenic in the sand layer of the study area after 10 years of its injection. Fig. 7.10 illustrates the distribution of arsenic in the sand layer of the study area after 15 years of its injection. Fig. 7.12 illustrates the distribution of arsenic in the sand layer of the study area after 20 years of its injection.

Table 7.4 gives the concentration of arsenic in the sand layer of the study area after 1 year of injection of arsenic, at every cell 4 kms apart. Table 7.6 gives the concentration of arsenic in the sand layer of the study area after 5 years of injection of arsenic, at every cell 4 kms apart. Table 7.8 gives the concentration of arsenic in the sand layer of the study area after 10 years of injection of arsenic, at every cell 4 kms apart. Table 7.10 gives the concentration of arsenic in the sand layer of the study area after 15 years of injection of arsenic, at every cell 4 kms apart. Table 7.12 gives the concentration of arsenic in the sand layer of the study area after 20 years of injection of arsenic, at every cell 4 kms apart.

The concentration of arsenic in the study area shows an increasing trend, which shows that the arsenic is spreading over the whole of the study area. The arsenic concentration after 20 years of injection had the maximum value as compared to the values after 1, 5, 10 and 15 years.

The arsenic concentrations in the clay layer were higher than the arsenic concentrations in the sand layer at almost all nodes. But the arsenic concentrations of the sand layer in the periphery of the study area were more than that of the clay layer. This shows that arsenic moves faster in the sand layer, which may be the reason why a larger concentration of arsenic is seen in the periphery of the study area. This may be due to the larger longituidinal dispersivity value of the sand layer. Thus it can be deduced that sand layer distributes the injected arsenic at a higher rate and more uniformly.

It was seen that Habra-II, southern part of Haringhata and western side of Habra-I has the maximum concentration of arsenic, followed by Baduria, Bangaon, Gaighata, Swarupnagar, Amdanga, Chakdah and Barackpore.

Cell No.	1	2	3	4	5	6	7	8	9	10	11	12	13
1	35.63	35.64	37.00	36.74	36.59	36.49	36.45	36.46	36.53	36.65	36.81	36.89	35.63
2	35.63	40.5	36.87	36.69	36.57	36.48	36.44	36.45	36.52	36.64	36.85	35.64	35.63
3	35.94	37.01	36.79	36.64	36.54	36.46	36.42	36.43	36.49	36.61	36.81	40.0	35.63
4	40.5	36.98	36.75	36.62	36.51	36.44	36.41	36.41	36.46	36.50	36.71	36.89	35.63
5	35.63	36.99	36.74	36.59	36.49	36.42	36.39	36.38	36.42	36.45	36.60	36.72	40.0
6	35.64	36.98	36.72	36.58	36.48	36.40	36.36	36.36	36.38	36.40	36.50	36.57	36.64
7	40.5	36.93	36.70	36.56	36.47	36.39	36.35	36.34	36.35	36.36	36.43	36.47	36.50
8	37.04	36.88	36.68	36.55	36.46	36.38	36.34	36.33	36.33	36.35	36.40	36.42	36.44

Table 7.1 Variation of hydraulic heads (m) in the clay layer (1st layer).

Cell No.	1	2	3	4	5	6	7	8	9	10	11	12	13
1	39.52	39.8	40.08	39.22	38.73	38.42	38.29	38.33	38.54	38.93	39.48	40.0	38.95
2	40.11	40.5	39.65	39.09	38.67	38.39	38.27	38.31	38.52	38.92	39.58	39.68	39.92
3	39.81	40.11	39.38	38.92	38.57	38.32	38.21	38.24	38.43	38.81	39.45	40.0	39.35
4	40.5	40.31	39.27	38.83	38.50	38.26	38.14	38.16	38.32	38.64	39.15	39.72	39.54
5	40.20	40.5	39.21	38.75	38.43	38.19	38.07	38.07	38.18	38.41	38.77	39.18	40.0
6	40.26	40.5	39.16	3870	38.38	38.14	38.01	37.98	38.05	38.22	38.45	38.35	38.91
7	40.5	40.22	39.09	38.65	38.34	38.10	37.96	37.92	37.96	38.07	38.22	38.35	38.45
8	40.21	39.99	39.04	38.63	38.32	38.08	37.94	37.89	37.92	38.01	38.12	38.21	38.27

Table 7.2 Variation of hydraulic heads (m) in the sand layer (2nd layer).

Cell No.	1	2	3	4	5	6	7	8	9	10	11	12	13
1	0	2.2×10^{-6}	60028.7	60022.1	60018.4	60016.0	60015.0	145037.1	145041	145048.2	145058.4	3.3×10^{-3}	0
2	4.2×10^{-18}	3.2×10^{-3}	60025.5	60021.1	60018.0	60015.9	60014.8	145036.7	145040.6	145048.1	145060.2	3.5×10^{-6}	0
3	2.2×10^{-5}	60029.0	60023.4	38512.7	38511.0	38511.0	38509.1	145035.7	145038.9	145046.0	145057.7	1.7×10^{-3}	0
4	8.0×10^{-4}	60028.2	60022.6	38512.3	38510.0	38509.5	38508.9	145033.9	145036.9	145042.8	145052.1	145062.9	2.4×10^{-15}
5	1.1×10^{-15}	60028.4	60028.4	75023.2	38509.6	38509.1	38508.5	145032.2	145034.3	145038.6	145045.4	145052.9	1.8×10^{-2}
6	1.5×10^{-15}	60028.	60028.2	75022.7	615150.3	615141.9	615132.0	35007.43	35007.71	35008.41	70020.4	70020.4	70023.1
7	1.8×10^{-3}	60027.0	60027.0	75022.3	615147.7	35008.2	35007.3	35007.1	35007.34	205045.5	205049.4	202049.4	70018.9
8	60029.8	60025.9	60025.9	75021.1	615145.9	615137.8	350072.2	35007.0	35007.16	205043.8	202046.8	205046.8	70017.4

Table 7.3 Concentration of arsenic ($\mu g/m^3$) in the clay layer (1st layer) after 1 year.

Cell No.	1	2	3	4	5	6	7	8	9	10	11	12	13
1	1.1×10^{-28}	1.8×10^{-5}	59987.9	60000.1	60000.0	60000.0	60000.1	145000.0	145000.1	145000.1	145000.1	3.99	7.1×10^{-23}
2	2.3×10^{-16}	2.64	60000.1	60000.0	60000.1	60000.0	60000.0	145000.0	145000.1	145000.1	144999.7	1.5×10^{-5}	5.6×10^{-27}
3	6.1×10^{-3}	59999.6	60000.1	38500.0	38499.9	38500.2	38500.1	145000.0	145000.0	145000.0	144998.2	2.66	1.8×10^{-19}
4	0.81	60000.1	60000.0	38500.0	38500.0	38500.0	38500.1	145000.0	145000.0	145000.1	145000.1	144997.6	5.2×10^{-10}
5	1.3×10^{-3}	59998.1	60000.0	74992.1	38502.0	38500.3	38500.1	145000.0	144999.8	144999.5	144999.4	144999.0	8.36
6	9.1×10^{-4}	59998.0	60000.0	75000.0	614992.6	615000.2	614997.3	35000.3	34999.8	35000.9	70000.4	70000.0	70000.0
7	1.26	59999.8	75000.1	75000.0	614992.3	35005.3	35000.0	35000.0	35000.3	205000.3	204998.3	70000.0	70000.0
8	59999.0	60000.4	75000.0	75071.9	615000.3	614996.3	35000.0	35000.0	35000.4	205000	205000.0	70000.5	69999.9

Table 7.4 Concentration of arsenic (μg/m^3) in the sand layer (2nd layer) after 1 year.

Cell No.	1	2	3	4	5	6	7	8	9	10	11	12	13
1	5.2×10^{-28}	1.1×10^{-5}	60137.6	60109.1	60091.2	60079.7	60074.9	145185.1	145203.9	145238.7	145288.7	0.147	6.0×10^{-24}
2	3.5×10^{-15}	0.14	60125.5	60104.6	60089.3	60078.6	60074.1	145182.9	145201.6	145237.9	145295.5	1.7×10^{-5}	1.3×10^{-27}
3	1.1×10^{-2}	60142.9	60115.8	38563.1	38554.8	38548.7	38545.9	145176.4	145193.5	145227.6	145283.8	7.6×10^{-2}	5.3×10^{-24}
4	3.6×10^{-2}	60139.2	60111.7	38560.9	38553.0	38547.2	38544.4	145169.4	145183.6	145212.2	145257.3	145308.7	3.7×10^{-11}
5	5.2×10^{-11}	60139.6	60109.3	75114.5	38551.2	38545.1	38542.6	145160.6	145170.8	145191.8	145224.1	145260.1	0.80
6	7.9×10^{-11}	60138.4	60107.2	75112.7	615798.2	615706.8	615658.6	35037.1	35038.4	35041.8	70094.1	70104.1	70113.8
7	8.1×10^{-2}	60133.1	75131.0	75110.6	615783.5	35050.8	35036.4	35035.5	35036.6	205226.9	205245.9	70089.8	70094.1
8	60147.5	60128.1	75128.9	75108.0	615778.2	615686.4	35035.9	35034.9	35035.8	205218.6	205233.8	70083.7	70086.9

Table 7.5 Concentration of arsenic (μg/m^3) in the clay layer (1st layer) after 5 years.

Cell No.	1	2	3	4	5	6	7	8	9	10	11	12	13
1	1.7×10^{-27}	1.5×10^{-3}	59948.7	60002.7	60001.3	60000.6	60000.5	145000.8	145002.1	145004.0	145006.1	19.59	7.0×10^{-19}
2	2.5×10^{-15}	12.8	60003.2	60002.1	60001.4	60000.6	60000.5	145000.8	145002.2	145004.3	144978.9	1.9×10^{-3}	1.3×10^{-16}
3	1.28	60001.5	60002.4	38501.1	38500.3	38501.1	38500.4	145000.8	145002.0	145004.1	144998.8	13.11	1.5×10^{-17}
4	4.00	60003.1	60002.1	38501.1	38500.6	38500.3	38500.6	145000.8	145001.7	145003.4	145006.4	144996.6	1×10^{-7}
5	0.82	59994.7	60002.2	74962.7	38510.6	38501.9	38500.8	145000.6	145000.3	145000.0	145001.0	145001.6	39.37
6	0.95	59994.4	60002.4	75001.7	614970.8	615004.8	614988.1	35001.7	34999.5	35004.9	70003.2	70001.8	70002.8
7	6.13	60002.2	75002.5	75001.6	614969.4	35026.6	35000.1	35000.0	35001.5	205002.6	204993.3	70002.3	70001.0
8	59997.6	60004.2	75002.3	75356.1	615008.1	614985.7	35000.1	35000.0	35002.2	205000.9	205001.0	70002.9	70000.2

Table 7.6 Concentration of arsenic (μg/m^3) in the sand layer (2nd layer) after 5 years.

Cell No.	1	2	3	4	5	6	7	8	9	10	11	12	13
1	1.2×10^{-26}	$2.2\times10\text{-}^{5}$	59747.9	60214.7	60180.6	60158.6	60149.8	145369.2	145404.8	145472.0	145569.0	0.61	1.4×10^{-22}
2	3.2×10^{-14}	0.59	60246.7	60206.3	60176.8	60156.4	60148.0	145364.8	145400.3	145469.8	145577.5	3.5×10^{-15}	3.0×10^{-26}
3	2.2×10^{-4}	60280.7	60228.3	38624.9	38608.7	38597.4	38591.7	145351.8	145384.3	145449.4	145556.0	0.31	1.2×10^{-22}
4	0.15	60274.3	60220.5	38620.7	38605.3	38593.9	38588.6	145337.8	145364.9	145419.6	145505.8	145604.2	3.5×10^{-10}
5	4.8×10^{-10}	60273.4	60215.5	75161.8	38601.9	38589.9	38584.9	145320.4	145339.9	145380.2	145442.1	145510.5	3.18
6	7.3×10^{-10}	60270.6	60211.5	75223.0	616584.1	616407.6	616314.9	35074.1	35076.5	35083.1	70186.4	70205.6	70223.8
7	0.33	60261.5	75258.5	75218.9	616555.0	35081.5	35072.7	35070.9	35073.1	205452.1	205489.0	70178.5	70186.7
8	60291.3	60252.8	75254.7	75220.9	616545.2	616366.8	35071.7	35069.8	35071.5	205436.2	205466.3	70167.0	70173.6

Table 7.7 Concentration of arsenic ($\mu g/m^3$) in the clay layer (1st layer) after 10 years.

Cell No.	1	2	3	4	5	6	7	8	9	10	11	12	13
1	9.1×10^{-25}	1.5×10^{-9}	40761.8	60011.0	60005.7	60002.5	60001.4	145003.5	145009.0	145016.6	145025.3	38.27	2.7×10^{-21}
2	7.3×10^{-13}	24.55	60013.1	60008.6	60005.4	60002.4	60001.3	145003.5	145009.1	145018.1	144978.6	6.1×10^{-5}	7.2×10^{-18}
3	5.3×10^{-7}	60010.3	60009.7	38506	38502.4	38503.0	38501.2	145003.5	145008.5	145017.2	145015.5	25.74	9.3×10^{-10}
4	7.83	60012.7	60008.9	38509	38502.1	38501.3	38501.4	145003.2	145007.3	145014.2	145026.2	145014.6	7.0×10^{-9}
5	6.0×10^{-5}	59998.6	60009.1	69864.6	38522.1	38504.5	38501.9	145002.5	145003.5	145005.5	145011.4	145018.2	73.22
6	3.1×10^{-4}	59998.4	60009.4	75007.1	614961.3	615020.2	614981.3	35003.6	34999.5	35010.6	70009.4	70007.7	70011.6
7	11.88	60011.9	75010.4	75006.7	614957.8	35053.4	35000.5	35000.2	35003.4	205008.3	204991.3	70006.5	70004.2
8	60001.4	60013.9	75009.5	75619.1	615033.9	614981.7	35000.5	35000.1	35004.6	205003.5	205004.2	70006.5	70000.8

Table 7.8 Concentration of arsenic (μg/m^3) in the sand layer (2nd layer) after 10 years.

Cell No.	1	2	3	4	5	6	7	8	9	10	11	12	13
1	6.7×10^{-26}	3.2×10^{-5}	58537.6	60316.8	60268.2	60236.6	60224.5	145552.2	145602.9	145700.2	145841.6	1.37	7.7×10^{-22}
2	1.1×10^{-13}	1.30	60363.9	60305.4	60262.8	60233.4	60221.8	145545.5	145596.0	145696.0	145335.3	5.2×10^{-5}	1.7×10^{-25}
3	3.3×10^{-4}	60413.9	60337.9	38685.3	38661.7	38644.9	38637.4	145526.1	145572.3	145665.9	145817.4	0.72	6.8×10^{-22}
4	0.33	60442.6	60326.5	38679.3	38656.7	38640.3	38632.7	145505.3	145543.7	145622.6	145730.3	145887.8	1.2×10^{-9}
5	1.7×10^{-9}	0.99	60318.9	75136.8	38651.9	38634.3	38627.2	145479.3	145507.0	145565.2	145654.4	145751.9	6.84
6	2.5×10^{-9}	1.11	60312.9	75331.1	617357.6	617101.9	616968.0	35110.9	35114.3	35123.9	70277.1	70304.7	70330.2
7	0.74	60424.2	75382.8	75325.1	617314.7	35122.1	35108.8	35106.4	35109.5	205675.4	205729.3	70266.1	70278.0
8	60431.5	60407.3	75377.5	75337.4	617300.9	617040.6	35107.4	35104.7	35107.2	205652.7	205697.3	70250.0	70260.1

Table 7.9 Concentration of arsenic ($\mu g/m^3$) in the clay layer (1st layer) after 15 years.

Cell No.	1	2	3	4	5	6	7	8	9	10	11	12	13
1	1.0×10^{-23}	5.1×10^{-7}	42731.9	60024.8	60012.8	60005.8	60002.4	145008.0	145020.3	145037.2	145056.5	56.07	5.3×10^{-19}
2	1.1×10^{-11}	1.1×10^{-4}	60029.2	60019.2	60011.9	60005.5	60002.2	145008.1	145020.6	145040.5	124970.1	0.57	1.3×10^{-16}
3	9.1×10^{-5}	48817.9	60021.6	38512.0	38505.3	38505.6	38502.2	145008.0	145019.2	145038.6	145030.0	37.91	8.1×10^{-7}
4	11.51	60028.4	60020.1	38518.2	3850536	38503.0	38502.6	145007.2	145016.6	145032.0	145058.3	145049.9	9.9×10^{-5}
5	1.7×10^{-3}	60010.7	60020.5	68639.4	38534.6	38507.6	38503.2	145005.8	145009.5	145016.1	145030.4	145048	101.49
6	2.9×10^{-4}	60011.0	60020.9	75015.9	614970.7	615045.7	614979.1	35005.8	34999.9	35016.9	70018.0	70017.3	70025.0
7	17.29	60028.3	75023.3	75015.1	614964.6	35080.4	35001.2	35000.6	35005.5	205016.8	204993.7	70012.4	70005.2
8	60010.9	60028.6	75021.2	75916.5	615076.8	614987.8	35001.1	35000.2	35007.1	205008.0	205009.7	70010.8	70001.8

Table 7.10 Concentration of arsenic (μg/m^3) in the sand layer (2nd layer) after 15 years.

Cell no.	1	2	3	4	5	6	7	8	9	10	11	12	13
1	2.2×10^{-25}	4.3×10^{-5}	57361.5	60416.0	60354.2	60314.0	60299.2	145734.3	145798.3	145923.6	146107.2	2.40	2.6×10^{-21}
2	2.7×10^{-13}	2.25	60477.7	60402.1	60347.4	60309.7	60295.5	145725.3	145789.1	145917.2	144728.0	7.0×10^{-5}	5.6×10^{-25}
3	4.5×10^{-4}	60543	60444.9	38744.6	38714.0	38692.4	38683.0	145699.5	145757.3	145877.5	146069.1	1.26	2.2×10^{-21}
4	0.58	60533.3	60430.5	38735.1	38707.4	38686.3	38676.7	145671.9	145720.6	145821.5	145980.1	146161.2	2.9×10^{-9}
5	4.0×10^{-9}	60502.7	60419.9	75105.2	38701.49	38678.3	38669.3	145637.8	145672.6	145747.2	145861.7	145985.4	11.43
6	6.0×10^{-9}	60325.1	60411.8	75437.3	618120.1	617790.6	617619.1	35147.8	35151.9	35164.4	70366.34	70401.7	70734.7
7	1.29	60505.7	75504.2	75429.5	618063.1	35162.6	35144.1	35141.7	35145.7	205897.0	205967.1	70352.7	70368.1
8	60568.4	60492.9	75497.7	75457.9	618047.3	617708.5	35142.9	35139.6	35142.8	205868.3	205927.6	70332.7	70346.4

Table 7.11 Concentration of arsenic (μg/m^3) in the clay layer (1st layer) after 20 years.

Cell no.	1	2	3	4	5	6	7	8	9	10	11	12	13
1	1.5×10^{-21}	1.8×10^{-3}	38952.5	60042.9	60022.6	60010.3	60003.7	145014.2	145036.0	145065.4	145085.9	73.08	1.8×10^{-15}
2	7.2×10^{-9}	45.36	60051.6	60033.9	60020.8	60009.8	60003.7	145014.4	145036.5	145071.1	126283.3	1.29	8.5×10^{-9}
3	9.5×10^{-3}	60047.7	60037.9	38519.7	38509.7	38508.8	38503.4	145014.2	145034.1	145067.8	145073.7	46.92	6.2×10^{-4}
4	15.0	60049.7	60035.3	38516.3	38509.9	38505.4	38504.0	145012.9	145029.4	145056.3	145104.3	145103.9	1.7×10^{-3}
5	8.1×10^{-4}	48065.2	60037.4	68840.2	38548.6	3851104	38504.9	145010.3	145018.3	145031.7	145057.6	145088.6	121.67
6	1.9×10^{-5}	48319.9	60037.9	75028.0	614998.4	615081.1	614982.1	35008.2	35000.9	35024.1	70029.1	70030.4	70293.9
7	22.4	60050.6	75039.2	75026.5	614989.0	35107.6	35002.1	35001.0	35007.8	205028.3	205000.3	70020.0	70016.9
8	60025.7	60048.0	75037.4	76204.6	615135.9	615003.8	35002.0	35000.3	35009.8	205014.2	205017.3	70015.56	70003.2

Table 7.12 Concentration of arsenic (μg/m^3) in the sand layer (2nd layer) after 20 years.

Fig. 7.1 Variation of hydraulic head in the clay layer (1st layer)

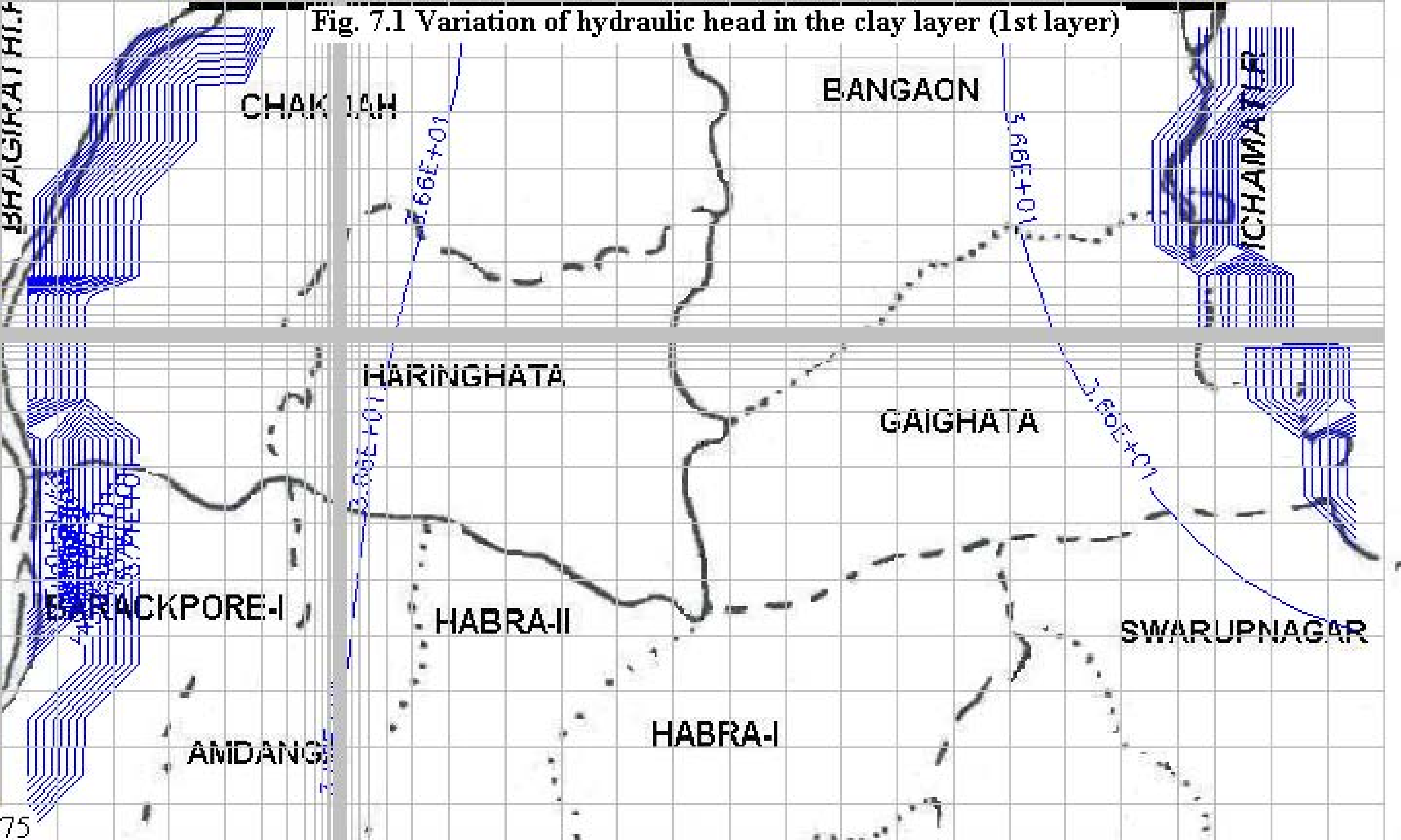


Fig. 7.2 Variation of hydraulic head in the sand layer (2nd layer)

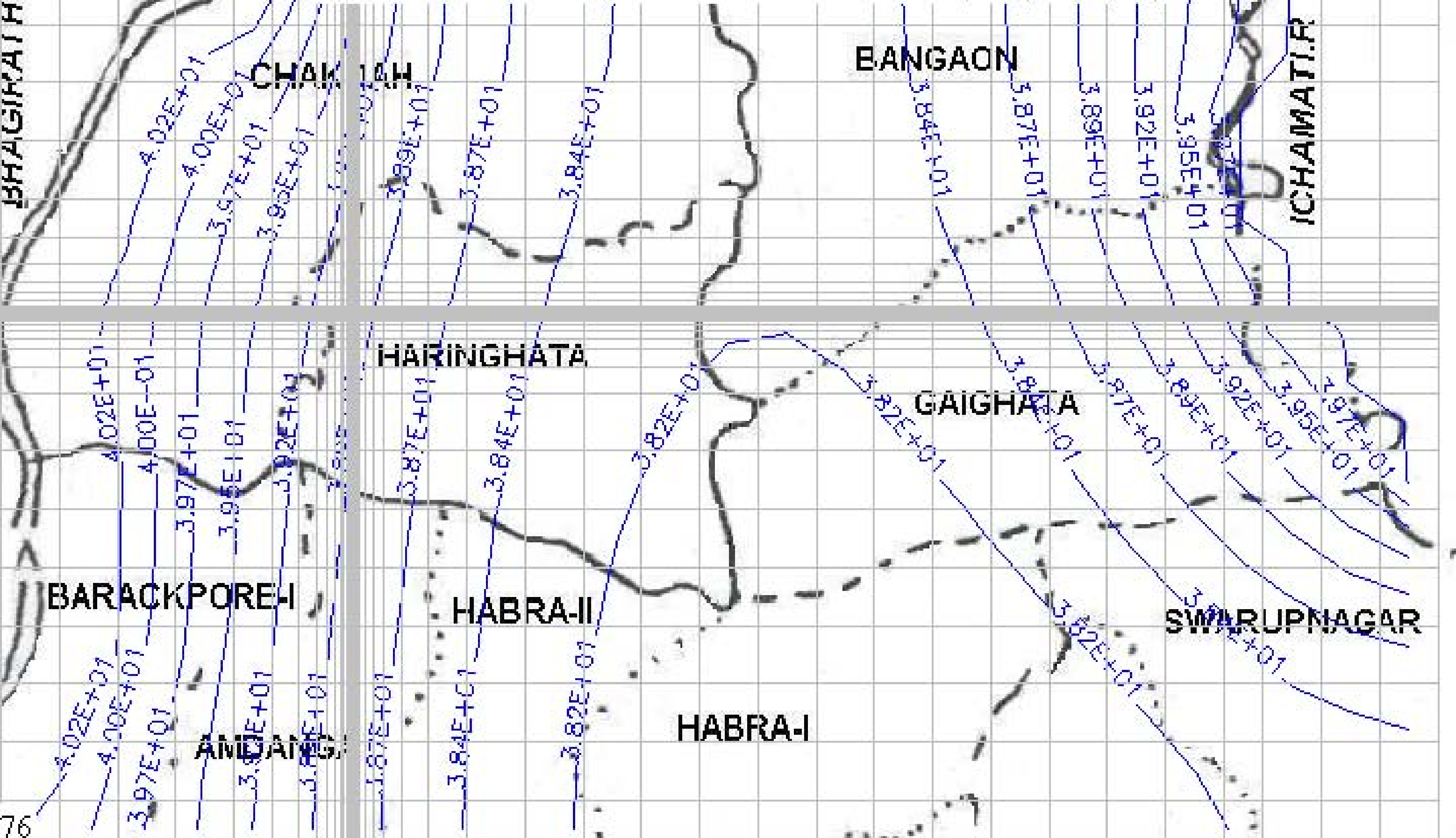


Fig. 7.3 Contour map showing distribution of arsenic in the clay layer (1st layer) after 1 year

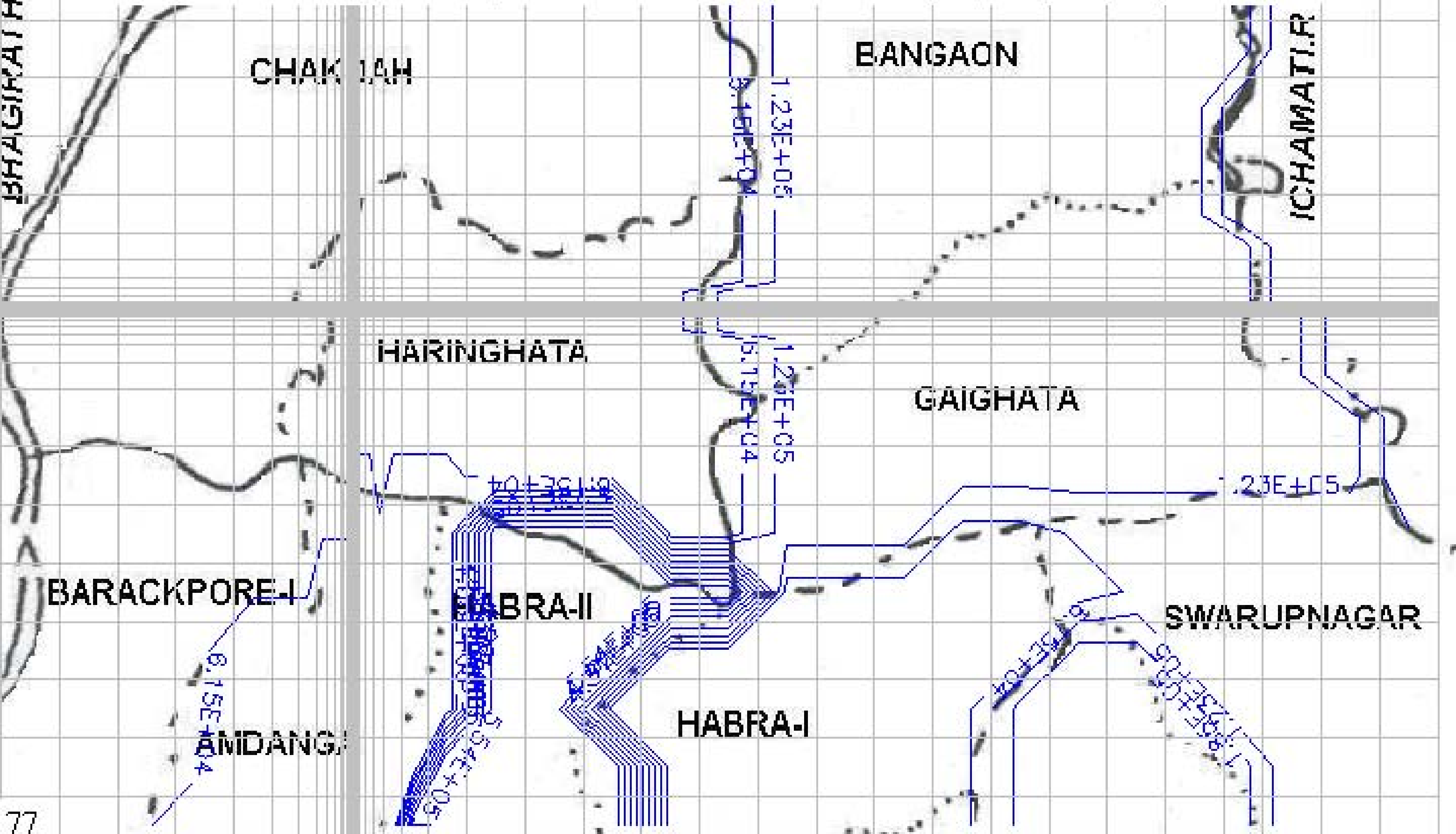


Fig. 7.4 Contour map showing distribution of arsenic in the sand layer (2nd layer) after 1 year

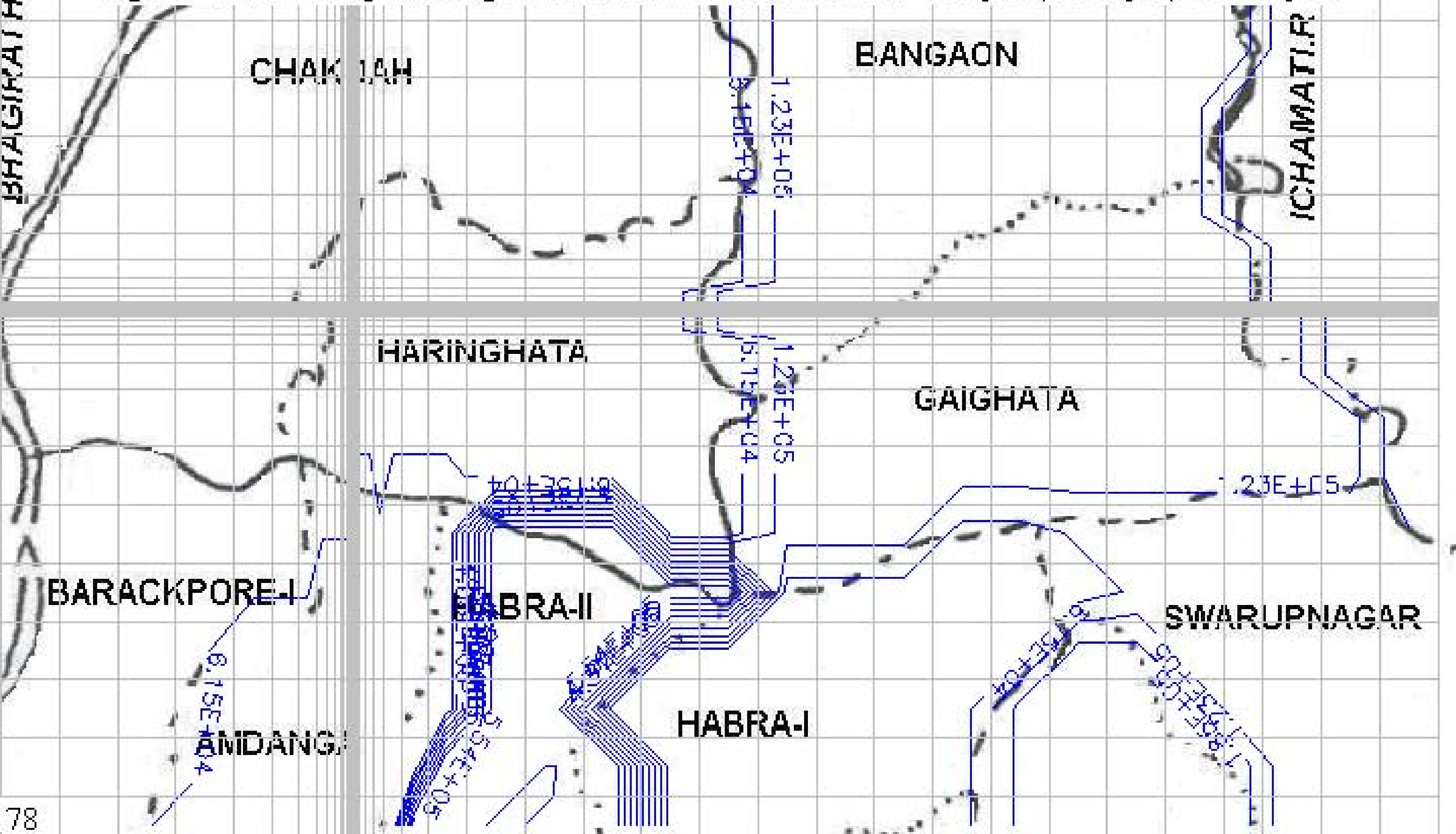


Fig. 7.5 Contour map showing distribution of arsenic in the clay layer (1st layer) after 5 years

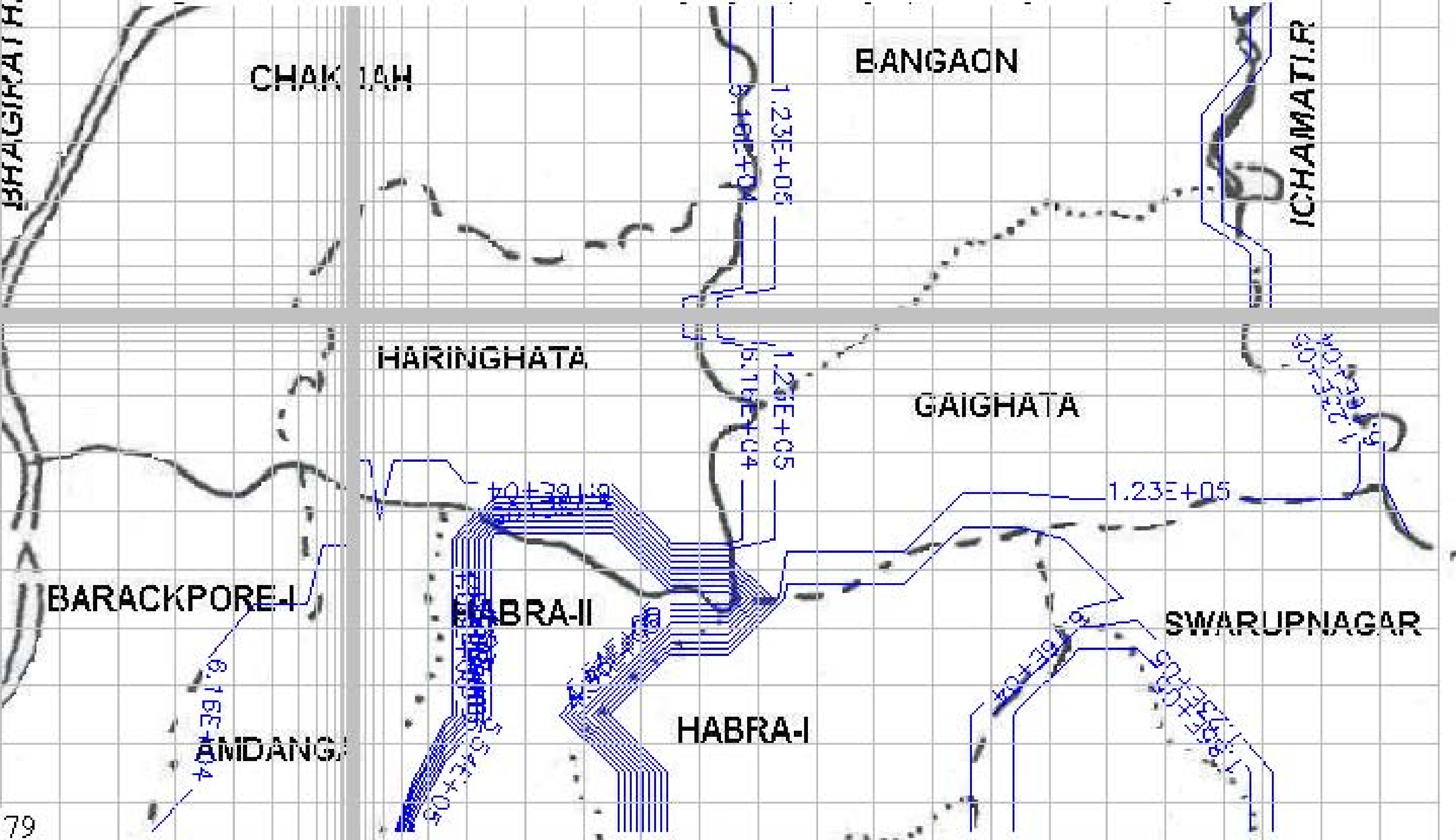


Fig. 7.6 Contour map showing distribution of arsenic in the sand layer (2nd layer) after 5 years

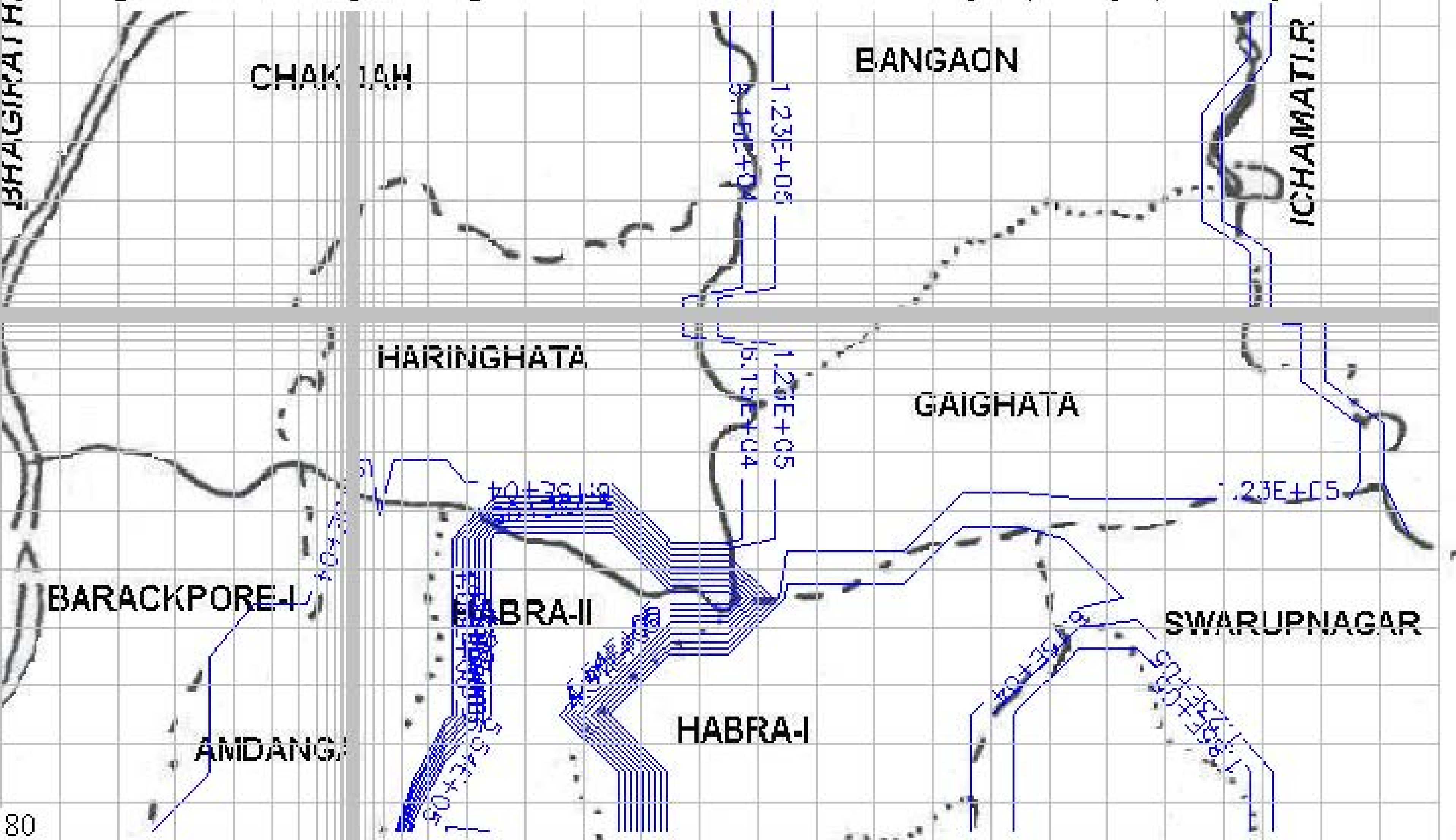


Fig. 7.7 Contour map showing distribution of arsenic in the clay layer (1st layer) after 10 years

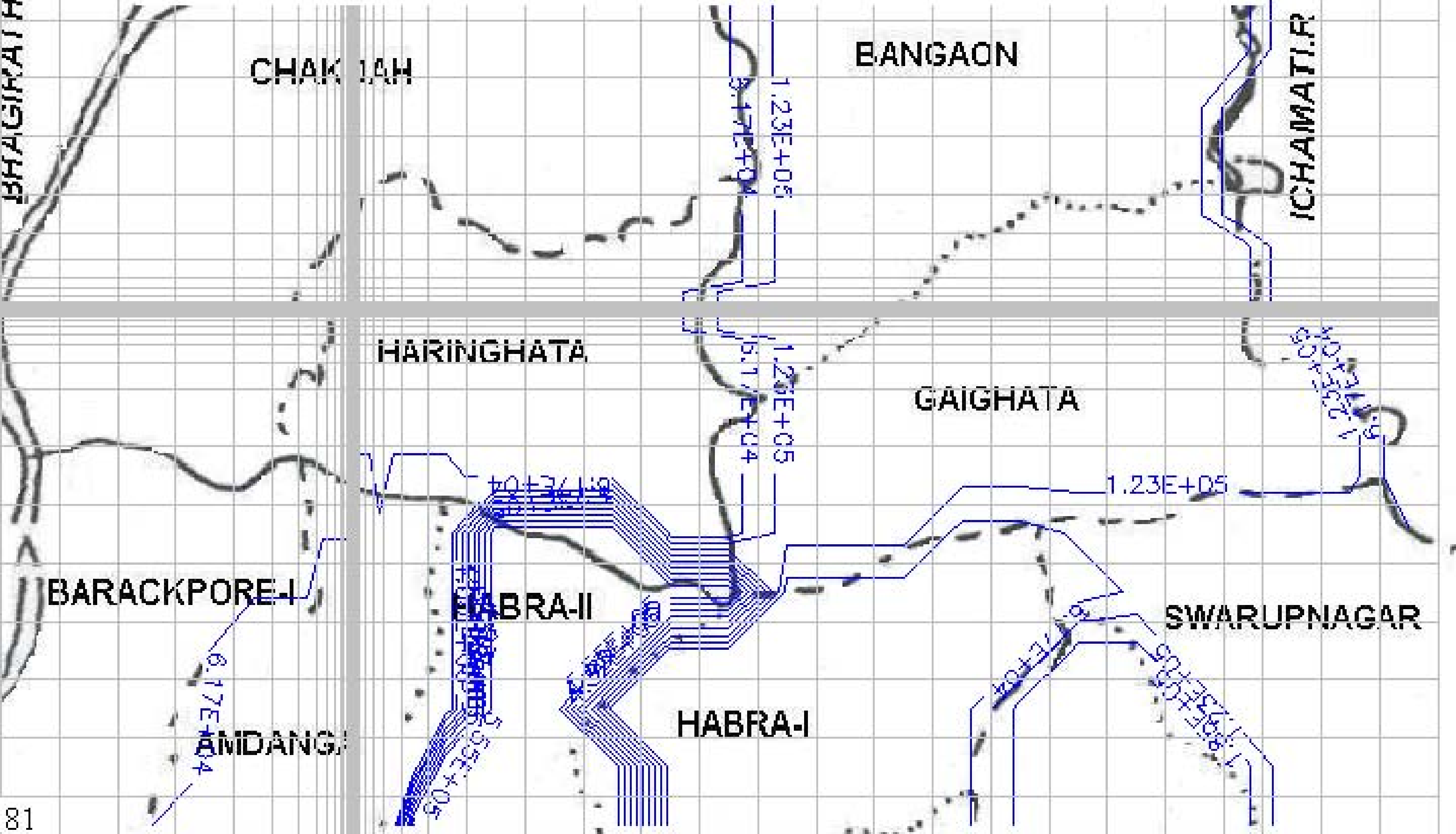


Fig. 7.8 Contour map showing distribution of arsenic in the sand layer (2nd layer) after 10 years

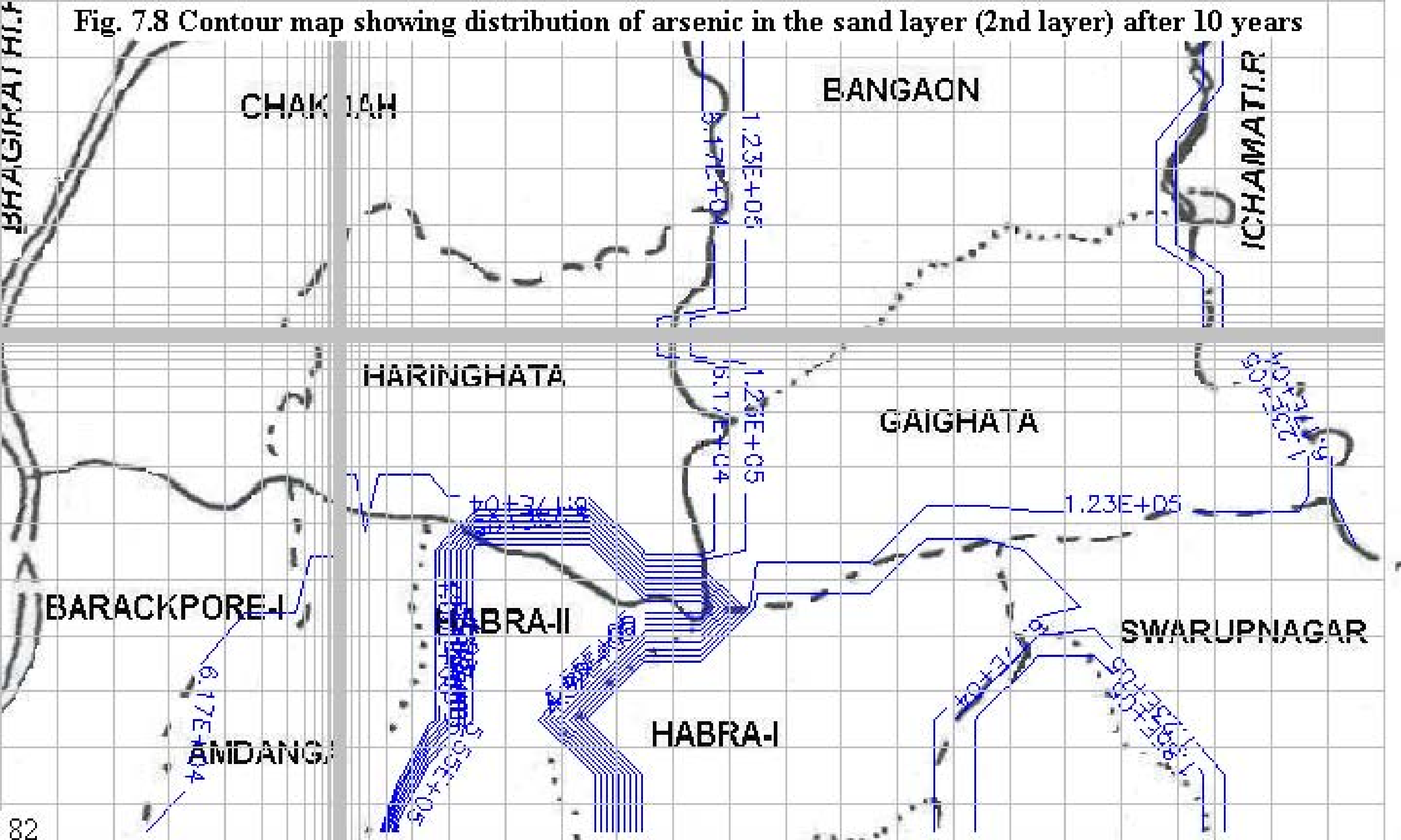


Fig. 7.9 Contour map showing distribution of arsenic in the clay layer (1st layer) after 15 years

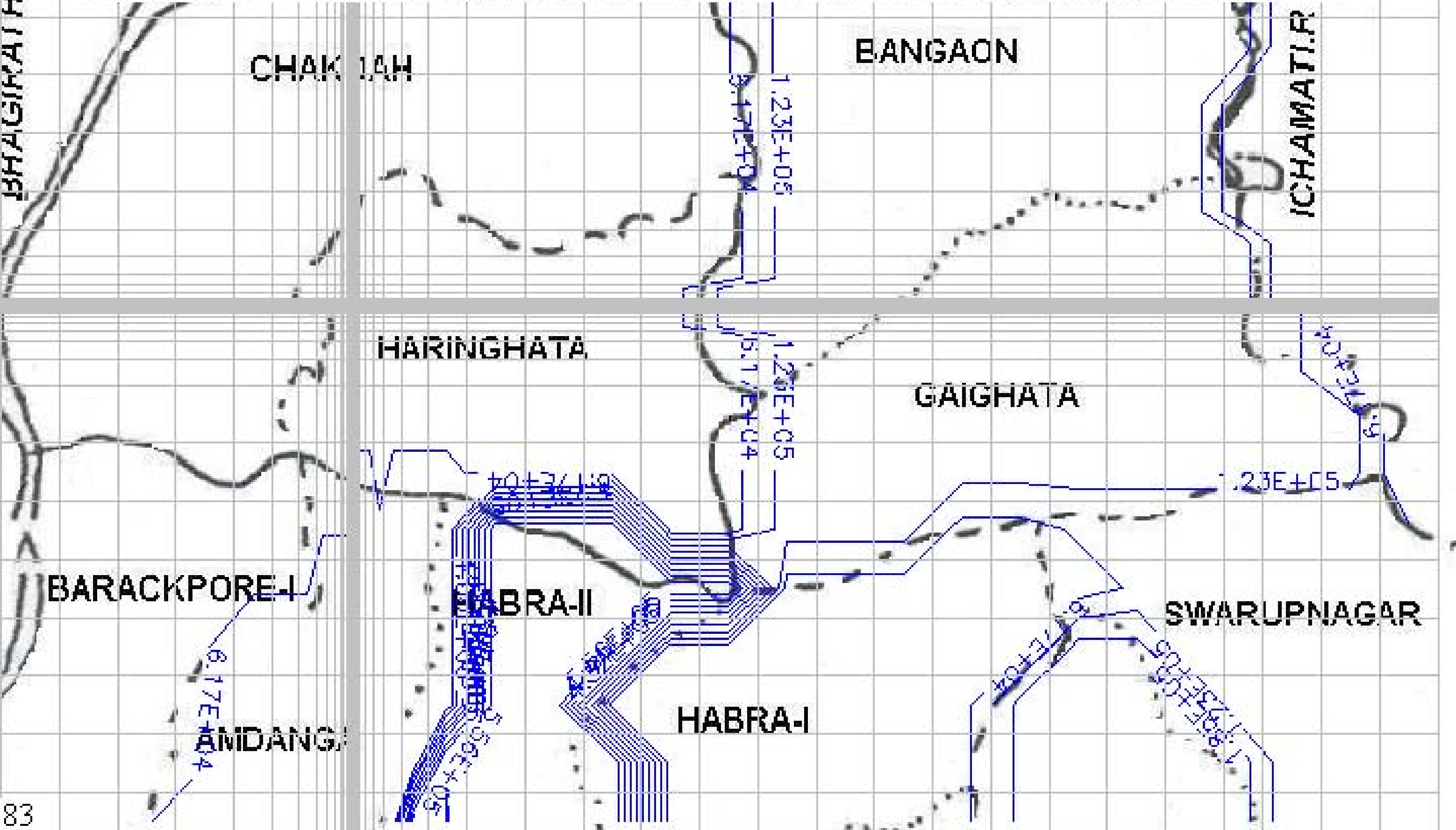


Fig. 7.10 Contour map showing distribution of arsenic in the sand layer (2nd layer) after 15 years

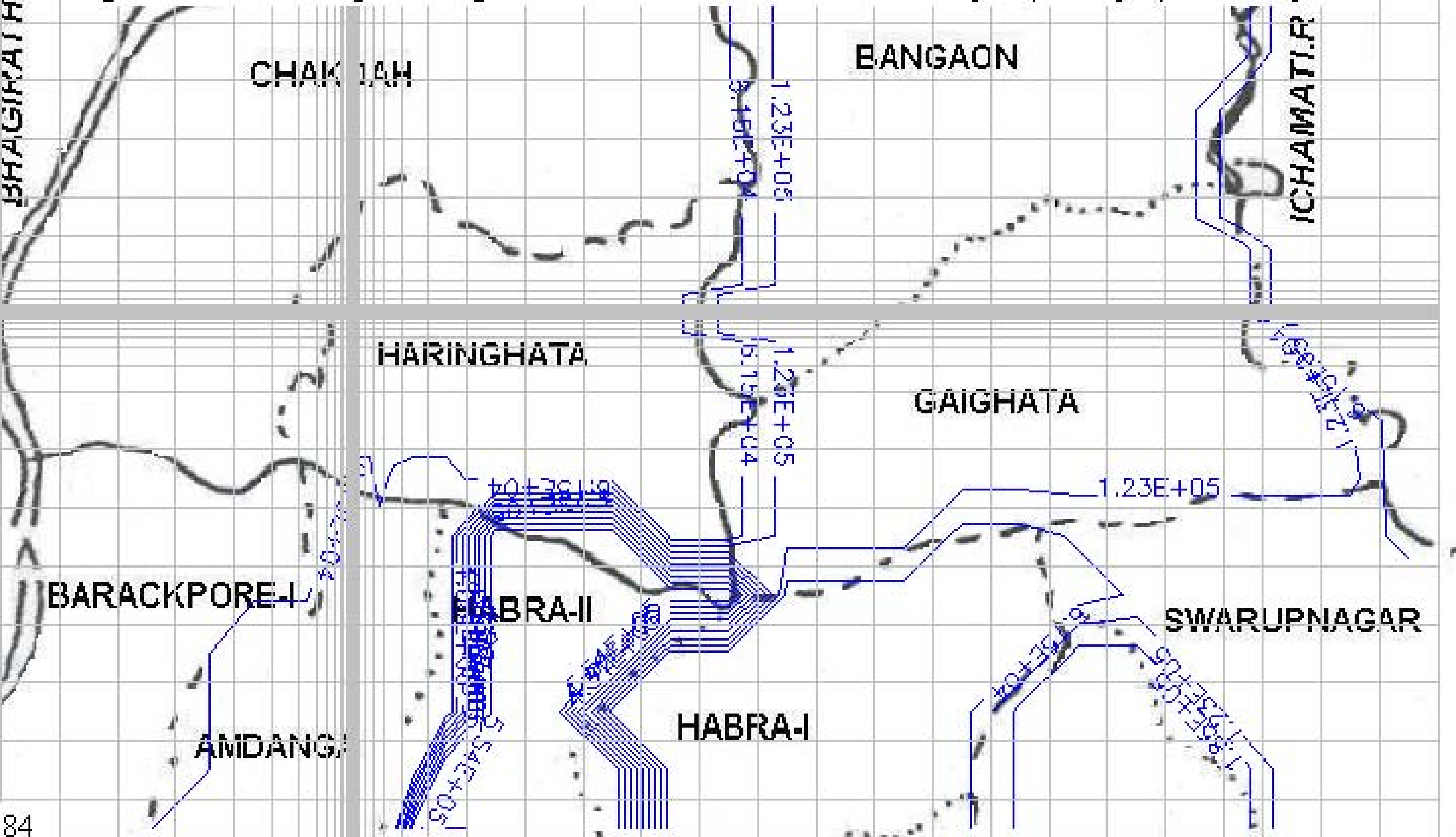
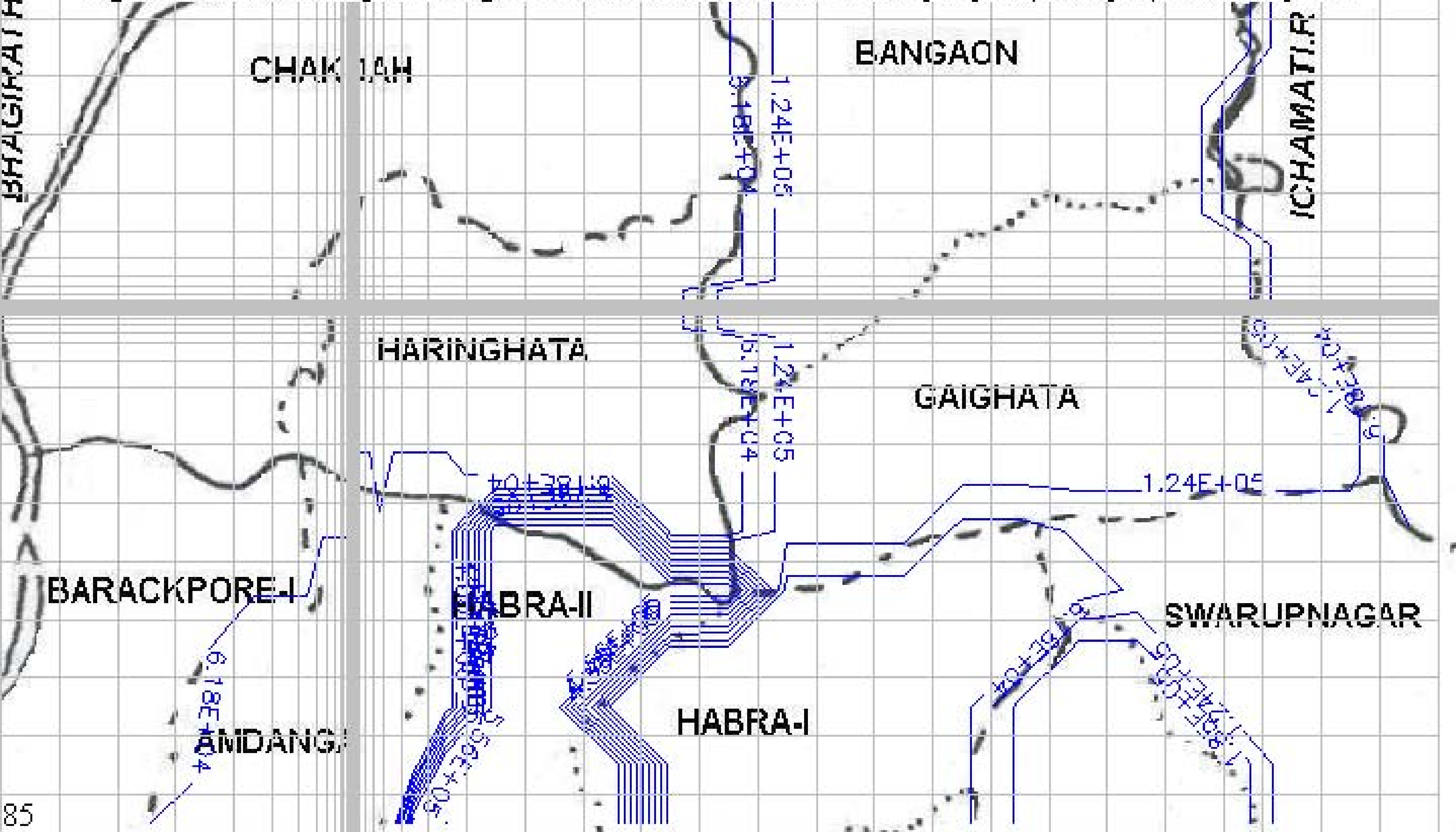


Fig. 7.11 Contour map showing distribution of arsenic in the clay layer (1st layer) after 20 years



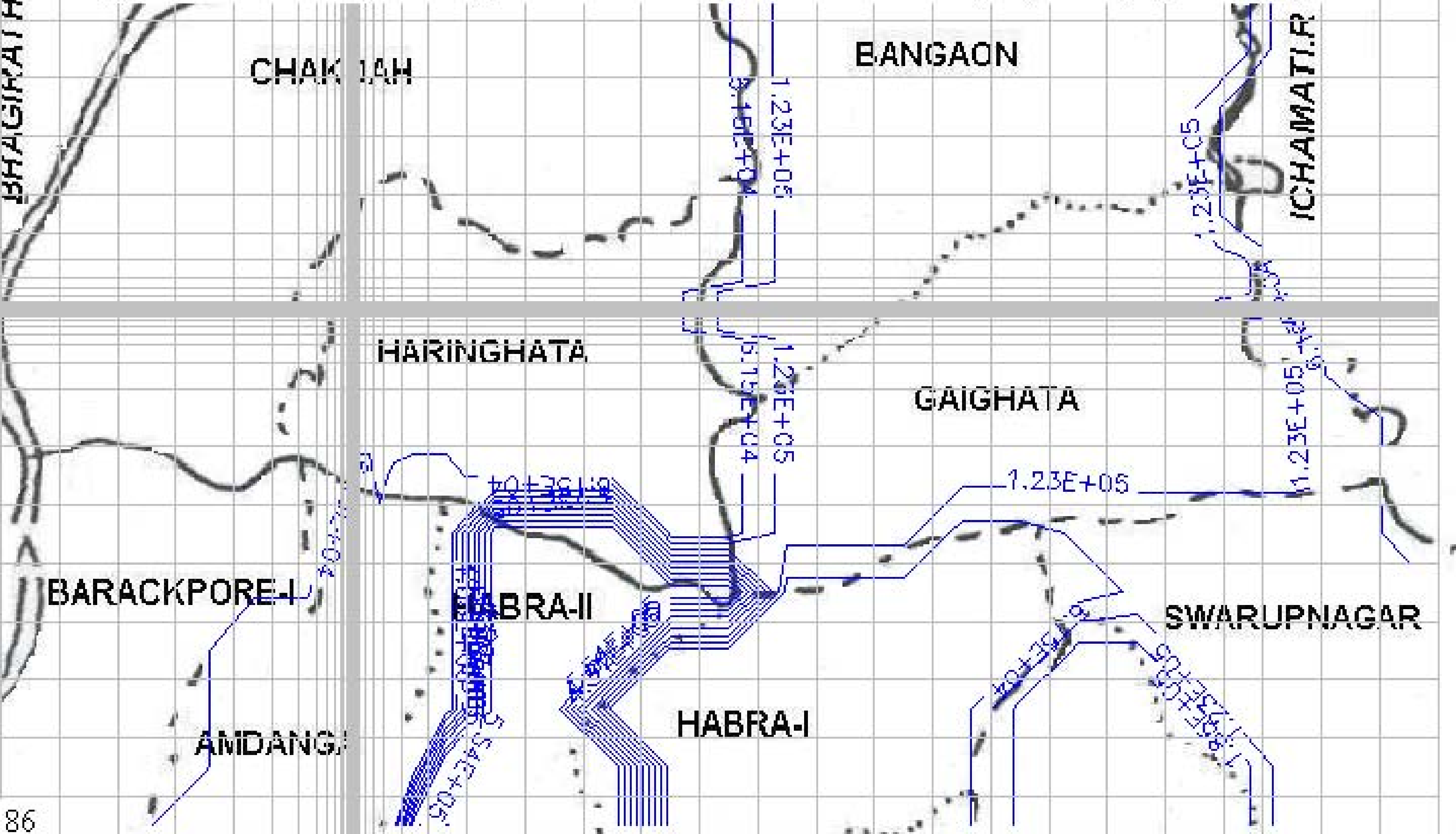


Fig. 7.12 Contour map showing distribution of arsenic in the sand layer (2nd layer) after 20 years

Fig. 7.13 Concentration of arsenic in borehole no. 1 vs Time

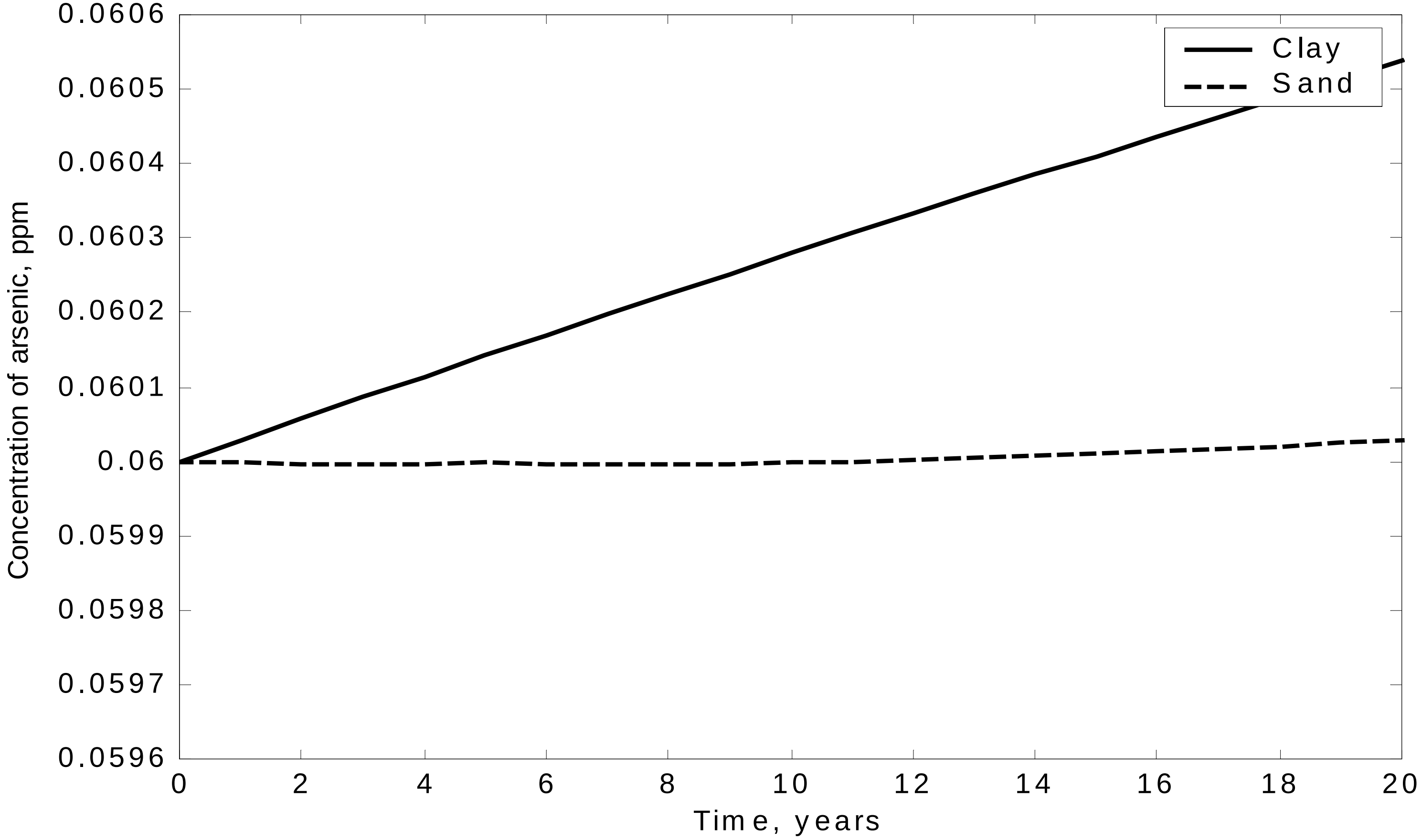


Fig. 7.14 Concentration of arsenic in borehole no. 2 vs Time

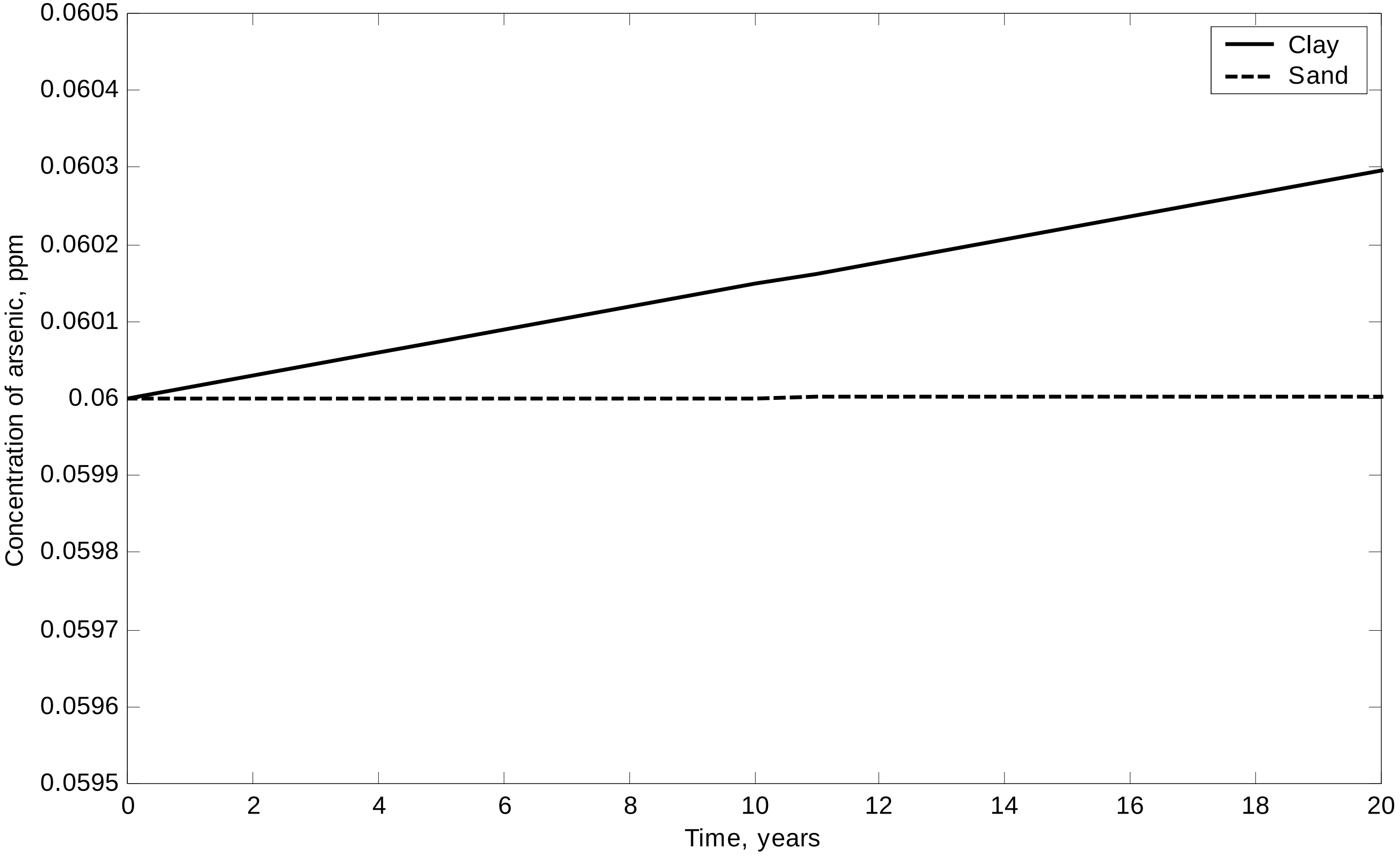


Fig. 7.15 Concentration of arsenic in borehole no. 3 vs Time

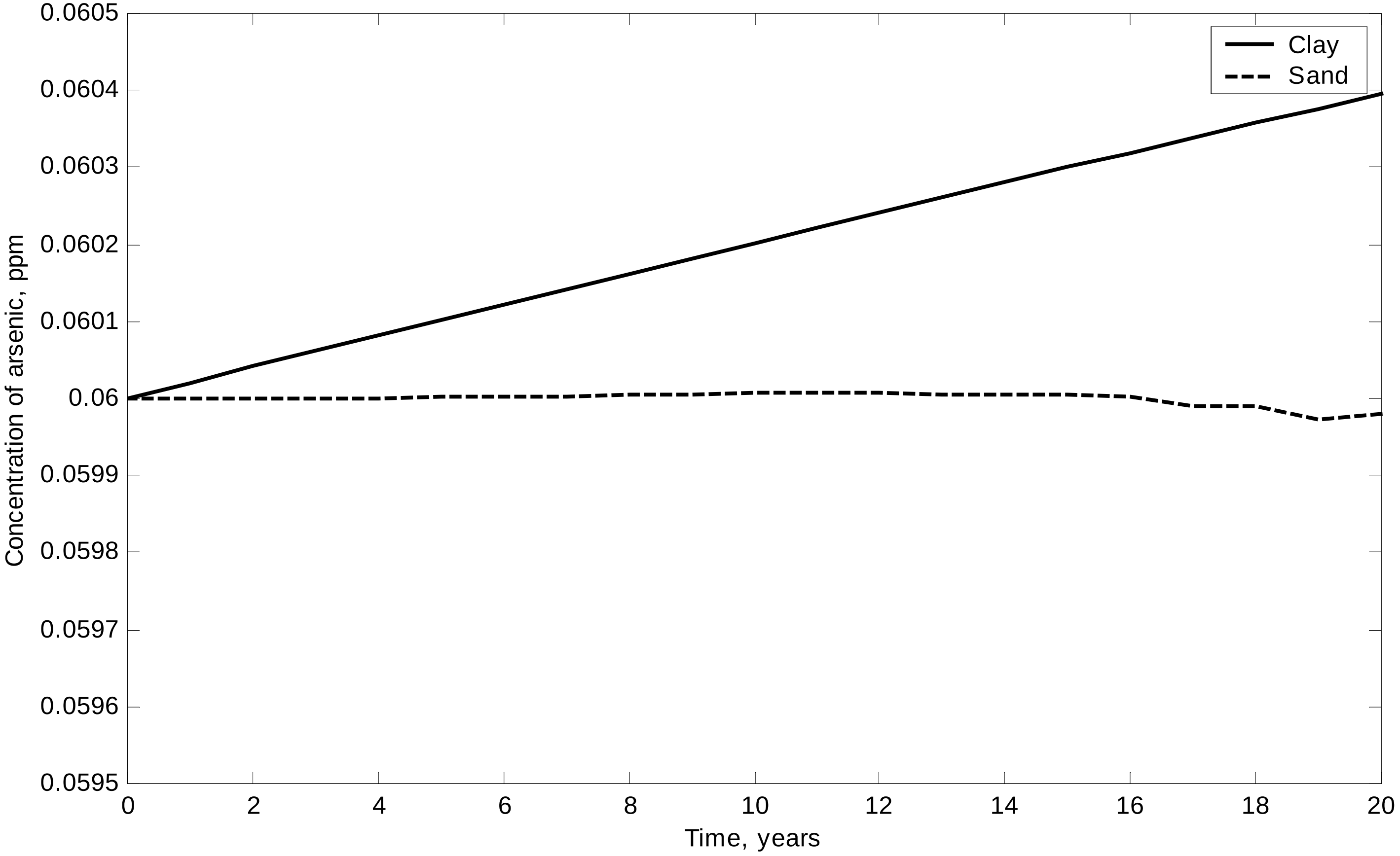
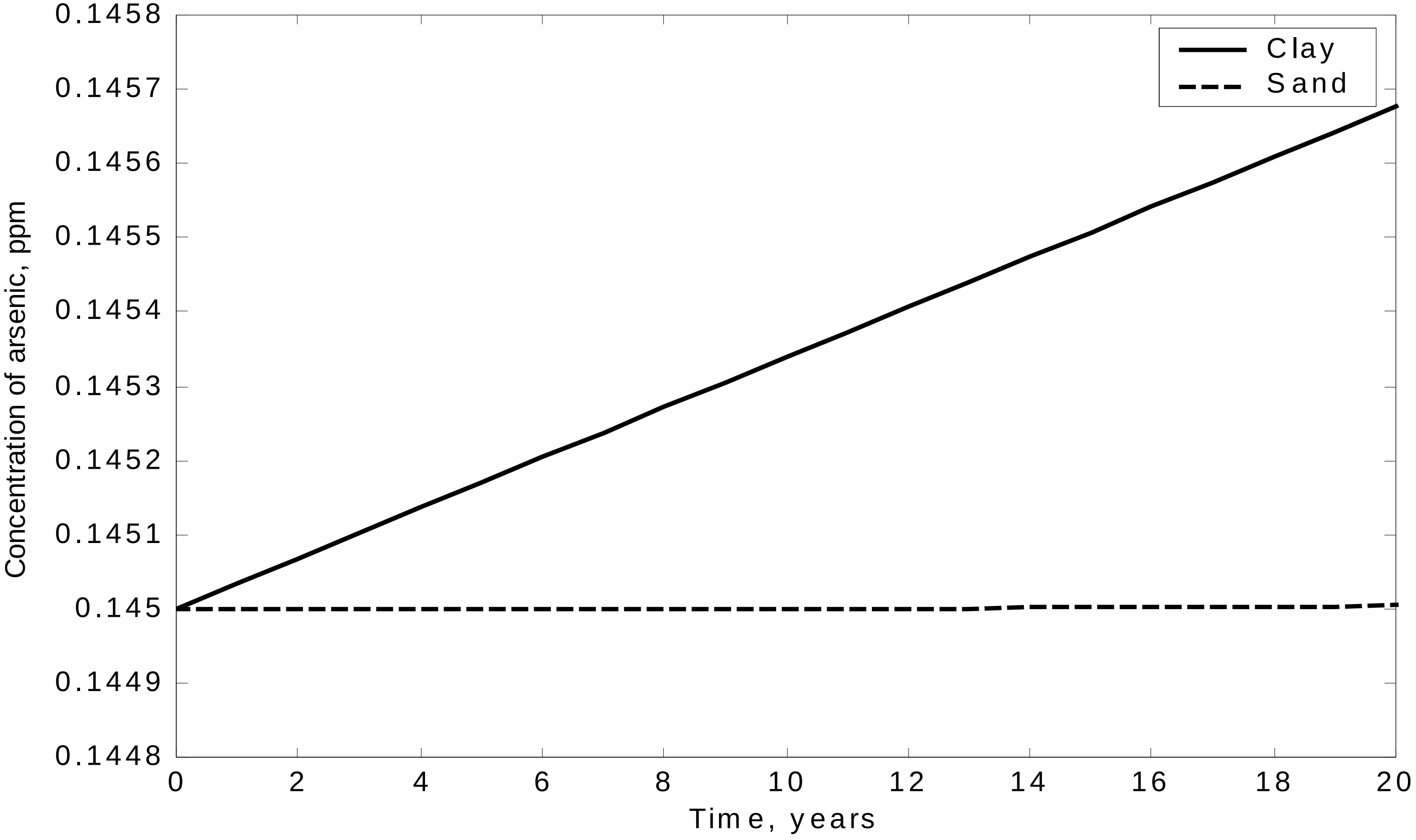


Fig. 7.16 Concentration of arsenic in borehole no. 4 vs Time



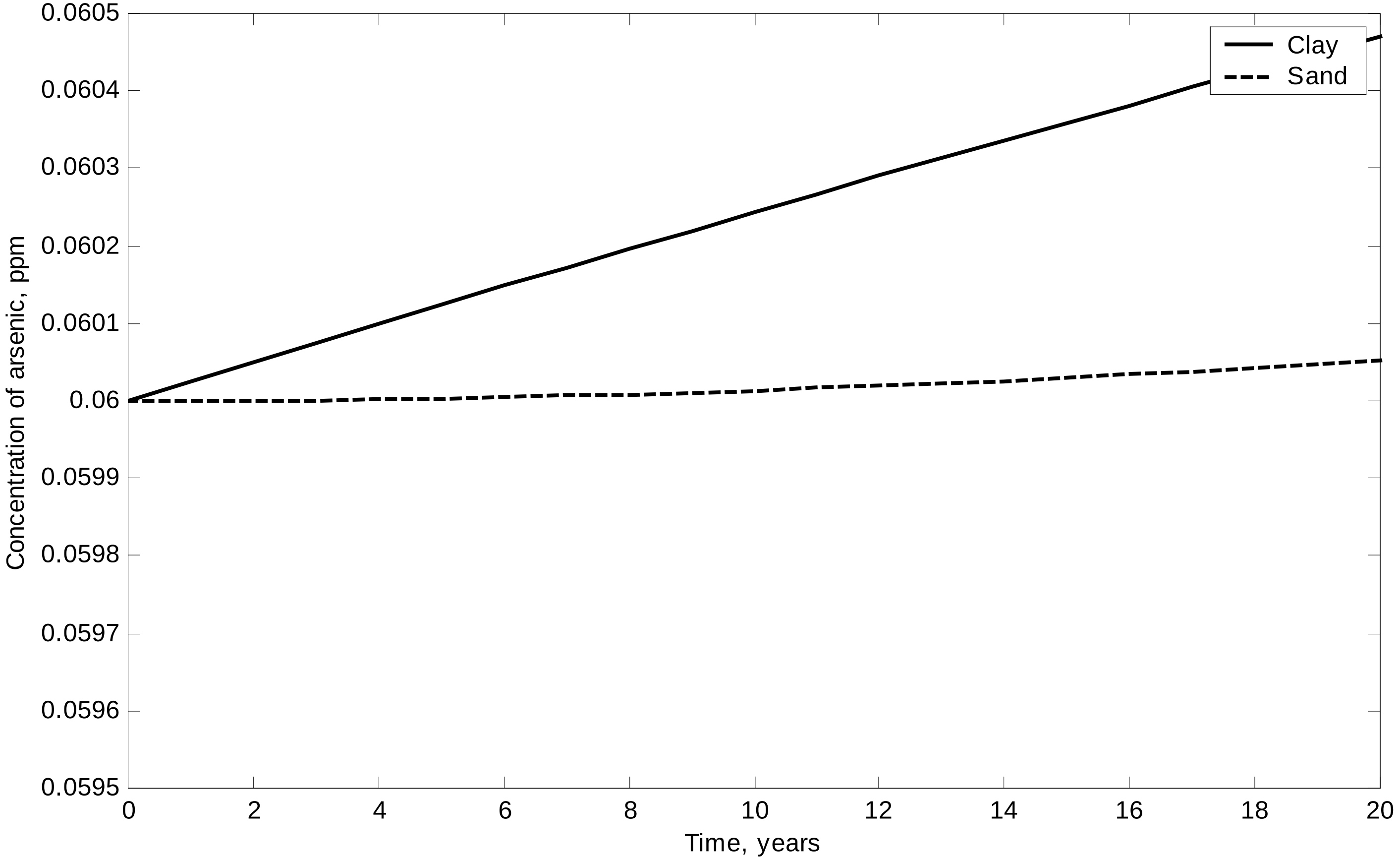
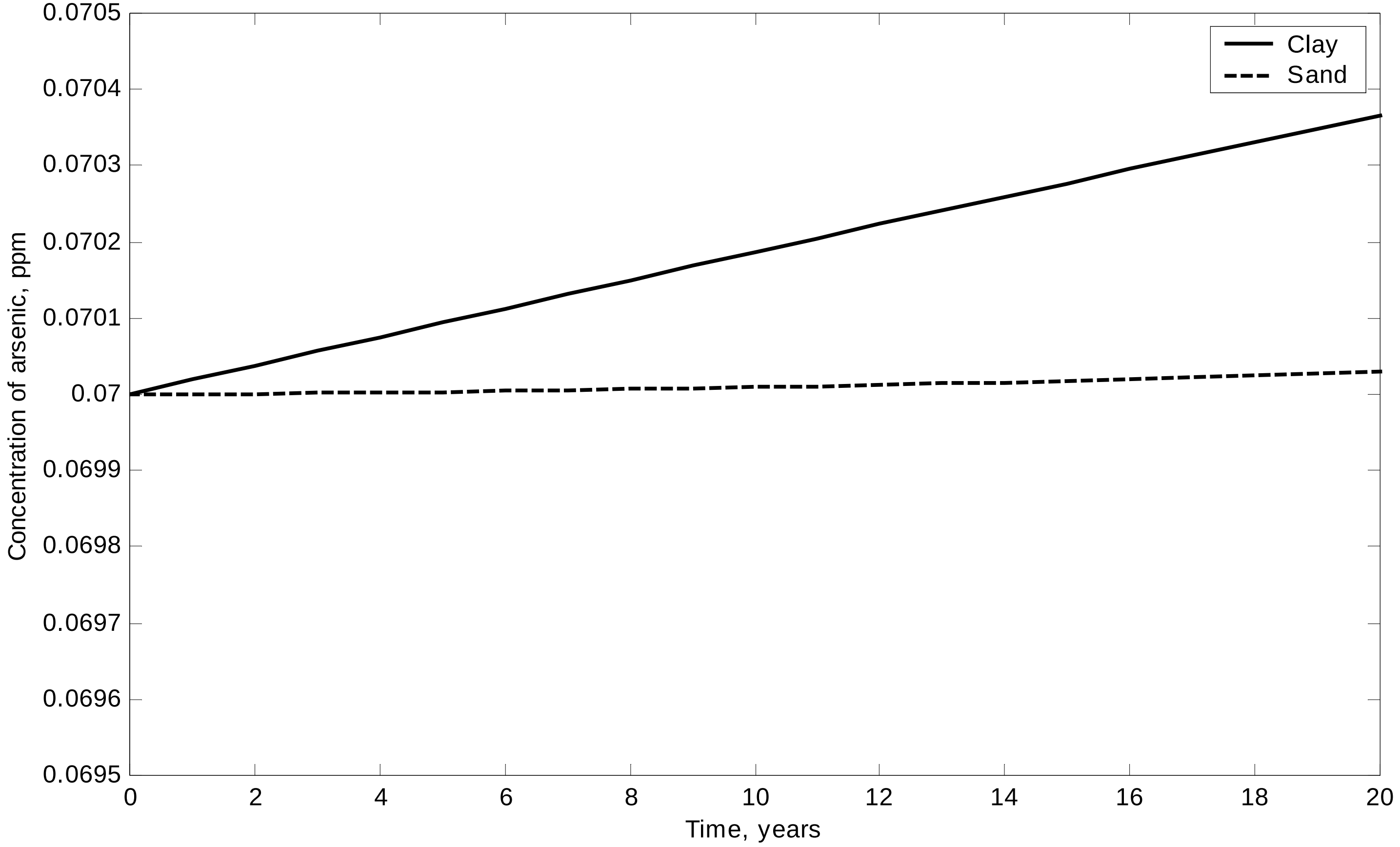


Fig. 7.17 Concentration of arsenic in borehole no. 5 vs Time

Fig. 7.18 Concentration of arsenic in borehole no. 6 vs Time



CONCLUSION

From the study the following conclusions were made:

- Arsenic pollution of groundwater is one of the World’s worst disasters affecting humans. But millions of people still drink arsenic contaminated water in the developing countries like India, Bangladesh etc. due to unavailability of other reliable source of drinking water. Long-term exposure to excessive arsenic causes changes in skin pigments and hyperkeratosis; promotes development of ulcerations of skin; and accelerates the risk of cancer in liver, bladder, kidney and skin.

- Microbial reduction of iron oxyhydroxide (FeOOH) and release of its sorbed arsenic load to solution is the main mechanism by which arsenic enters the groundwater. Shallow aquifers are relatively more prone to contamination by arsenic than deep aquifers.

- MODFLOW was successfully used to simulate three-dimensional groundwater flow and it revealed the variation of hydraulic heads in the study area. MT3D simulated the movement of arsenic in the study area for every 1 year for a stress period of 20 years and revealed the impact of injection of 100ppm of arsenic in the study area.

- There is a uniform distribution of the water that is recharged from the river in the sand layer of the study area whereas the clay layer is not able to distribute this water uniformly, due to its low hydraulic conductivity. Thus the hydraulic heads contour map for the sand layer is a gradual concave curve and the hydraulic heads contour map for the clay layer is a sharp concave curve with steep hydraulic gradient in the periphery and gentler slope towards the center.

- There is a spatial and temporal variation in the concentration of arsenic due to its injection at a point in the study area. The concentration of arsenic increases in the study area with time, with the 20 years concentration having the maximum value. Arsenic moves faster in the sand layer than in the clay layer, which is shown by the higher peripheral concentration of arsenic in the sand layer.

- Habra-II, southern part of Haringhata and western side of Habra-I have the maximum concentration of arsenic, followed by Baduria, Bangaon, Gaighata, Swarupnagar, Amdanga, Chakdah and Barackpore. Even though both Habra-I and Haringhata had a low initial arsenic concentration, because of the influx of arsenic from the neighbouring block of Habra-II, western side of Habra-I and the southern side of Haringhata was seen to have maximum arsenic concentration.

- The arsenic crisis may aggravate, affecting more and more area with the passage of time, the areas adjoining West Bengal and Bangladesh being the most susceptible. Places having sandy soil will be more susceptible to arsenic pollution by than places having clayey soil

RECOMMENDATIONS

Keeping in view the arsenic contamination of the groundwater in the study area, the following recommendations are suggested to contain the problem:

- Alternate sources of arsenic free safe drinking water should be provided.
- The people should be informed about the health risk associated with drinking arsenic contaminated water.
- A long-term groundwater, surface water and sediment-monitoring program should be established to monitor the arsenic behaviour in the region so that a proper remediation/ management program be undertaken and implemented.
- A good lab with the principal objective of studying arsenic transport and behavior in the region should be established.
- Large-scale piped water supply could be provided to the rural communites by drawing water from rivers and treating them for removal of pathogenic bacteria.
- Steps for conservation and quality upgradation of traditional surface water sources like ponds, dug-wells etc. in the villages should be undertaken. These sources are generally free from arsenic but grossly contaminated with faecal contamination.
- Arsenic from groundwater can be removed by using technologies like, adsorption (activated alumina), co-precipitation (oxidation, coagulation & filtration) or ion exchange. These technologies could be applied in community plants attached to hand pump tube-wells or large diameter tube-wells. Otherwise domestic filters could also be developed on the basis of these technologies.
- Immediate requirement for drinking and cooking purpose should be served from arsenic free water like water from deep tube wells. Other household works can be performed by pond, canal, river water or even by tube well water containing arsenic.
- To provide arsenic free drinking water as a long term solution some alternative approaches, for example, rainwater harvesting have been recommended

considering the availability of surface water, economic conditions, social acceptance and environmental soundness.

- Arsenic water is discharged into natural reservoirs directly after use, thereby contaminating the water of ponds, canals, ditches etc. If this practice continues, the safe source of surface water will be polluted in the near future. Therefore, it is urgently needed to stop the practice of discharging arsenic groundwater.
- Newly developed technologies, capable of removing arsenic from contaminated groundwater, produce a huge amount of arsenic rich sludge. This arsenic may contaminate the groundwater or be released into the atmosphere, if arsenic rich sludge is not manage properly. Therefore, more research should be conducted to manage arsenic rich sludge, so that the environment will not be affected anymore.

APPLICATIONS OF THE STUDY

The study deals with simulation of water and arsenic movement using a 3D solute transport model. The hydraulic heads of the groundwater in the study area were studied to understand the direction of flow of groundwater. It was assumed that arsenic was injected continuously at a point in the study area and its distribution and movement were studied.

The results of this study will be useful to individuals, municipalities, and regulators who all have an interest in maintaining safe drinking water supplies. An understanding of the mechanisms controlling arsenic contamination will be useful in modifying well construction methods and placing new wells to prevent contamination and in designing mitigation measures for already contaminated wells.

This study will be useful in understanding the difference in the movement of arsenic in soils like clay and sand. From this a mitigation scheme can be chopped out to control the spread of arsenic This study can also be manipulated to locate safe drinking water wells in the arsenic polluted groundwater in the study area. This can be done by locating areas and aquifer layers having permissible (least) arsenic in the groundwater.

FUTURE SCOPE OF WORK

Simulations of these types can be used as a tool to elicit and discern the detailed structure of evolving solute plumes that occur in realistic aquifer systems and to validate predictions of their large-scale behavior.

Future simulations of this sort with the experimentally determined hydraulic parameters of the aquifer will be very helpful in determining the arsenic polluted areas. Such similar models can also be applied to other regions of the world where there is contamination of the groundwater with other pollutants.

This model can be further developed to simulate movement of multi-species contaminants. Additional work can be carried out in systems characterized by different physical boundaries.

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APPENDIX-I

DISTRIBUTION OF ARSENIC IN THE STUDY AREA

Block-wise arsenic distribution in the groundwater for the Yamuna Sub-basin provided by the CGWB, Kolkatta (Unpublished Report) is given below in a tabular form.

District	Block	Depth (mbgl)	Arsenic (ppm)
Nadia	Chakdah	90-100	0.05-0.07
	Kaliganj	10-30 60-70	0.06-1.0 0.06-0.12
	Haringhata	10-50	.05-.027
N 24 Parganas	Habra I	12-45 150-185	0.05-0.02 0.05-1.0
	Habra II	15-75 110-135	0.05-1.18 0.05-1.16
	Barasat I	30-40	0.05-1.40
	Barasat II	30-45 80-110	0.05-0.2 0.05-0.8
	Baduria	20-45 96	0.05-0.36 0.12
	Amdanga	35-60 90	0.05-0.1 0.05-0.20
	Rajarhat	70-80	0.05-0.17
	Basirhat	75-85	0.05-0.19
	Gaighata	30-95	0.05-0.24
	Swarupnagar	15-70 100-130	0.05-0.09 0.05-0.92

APPENDIX-II

MODFLOW

U.S. GEOLOGICAL SURVEY MODULAR FINITE-DIFFERENCE GROUND WATER FLOW MODEL

```
THE FREE FORMAT OPTION HAS BEEN SELECTED
2 LAYERS        36 ROWS        46 COLUMNS
1 STRESS PERIOD(S) IN SIMULATION
MODEL TIME UNIT IS SECONDS

 LAYER                LAYER-TYPE CODE                INTERBLOCK T
 -----------------------------------------------------------------------------------------
     1                        2                       0 -- HARMONIC
     2                        0                       0 -- HARMONIC
```

STRESS PERIOD NO.   1

```
LENGTH =  0.6307000E+09
NUMBER OF TIME STEPS =
MULTIPLIER FOR DELT =     1.000
INITIAL TIME STEP SIZE =  0.6307000E+09

MAXIMUM HEAD CHANGE FOR EACH ITERATION (1 INDICATES THE
FIRST INNER ITERATION):

HEAD CHANGE  (LAYER,ROW,COL)      HEAD CHANGE  (LAYER,ROW,COL)
1       -3.785           ( 1, 11, 46)        0     1.133           ( 2,  5, 39)
0        0.3799          ( 2, 36, 41)        0     0.2656          ( 2, 13,  9)
0        0.1177          ( 2, 36, 35)        0     0.7419E-01      ( 2, 36, 33)
0        0.4349E-01      ( 1, 17, 17)        0     0.2060E-01      ( 1, 16,  6)
0        0.1341E-01      ( 1, 16, 39)        0     0.8737E-02      ( 1, 16, 37)
```

```
0      0.3896E-02     ( 1, 16, 35)          0     0.1722E-02        ( 1, 16, 37)
0      0.1065E-02     ( 1, 36, 16)          0     0.6735E-03        ( 1, 13, 13)
1     -0.1895E-03     ( 2, 15, 15)

MAXIMUM RESIDUAL FOR EACH ITERATION (1 INDICATES THE FIRST
INNER ITERATION):
RESIDUAL    (LAYER,ROW,COL)                 RESIDUAL    (LAYER,ROW,COL)
1    0.4460E-02      ( 2,  6, 43)            0    0.1521E-02       ( 2, 31, 46)
0    -0.1105E-02    ( 2,  7,  7)             0    -0.8350E-03      ( 2, 31, 45)
0    -0.4835E-03    ( 2, 31, 45)             0    -0.2077E-03      ( 2, 31, 45)
0    -0.9638E-04    ( 2,  2, 43)             0    0.6596E-04       ( 2, 35,  5)
0    0.3459E-04     ( 2, 32, 45)             0    -0.1596E-04      ( 2,  3, 42)
0   -0.1002E-04     ( 2,  3, 42)             0    0.6769E-05       ( 2, 31, 45)
0    0.4489E-05     ( 2, 31, 45)             0     0.2623E-05      ( 2, 31, 45)
1    0.1869E-05     ( 2, 31, 45)

VOLUMETRIC BUDGET FOR ENTIRE MODEL AT END OF TIME STEP  1 IN
STRESS PERIOD  1:

CUMULATIVE VOLUMES    L**3          RATES FOR THIS TIME STEP    L**3/T
                 IN:                                     IN:
CONSTANT HEAD =    64241388.0        CONSTANT HEAD =         0.1019
              WELLS =          0.0000                WELLS =         0.0000
                   ET =          0.0000                     ET =         0.0000
       RECHARGE =  2356840190.0000          RECHARGE =        3.7369
         TOTAL IN =  2421081600.0000           TOTAL IN =         3.8387

               OUT:                                     OUT:
CONSTANT HEAD =          0.0000         CONSTANT HEAD =         0.0000
             WELLS =      158492.7340              WELLS  =      2.5130E-04
                 ET  =  2420922110.0000                   ET =         3.8385
       RECHARGE =           0.0000          RECHARGE =         0.0000
```

TOTAL OUT = 2421080580.0000 TOTAL OUT = 3.8387

IN - OUT = 1024.0000 IN - OUT = 1.6689E-06

PERCENT DISCREPANCY = 0.00 PERCENT DISCREPANCY = 0.00

TIME SUMMARY AT END OF TIME STEP 1 IN STRESS PERIOD 1:

PARAMETERS	SECONDS	MINUTES	HOURS	DAYS	YEARS
TIME STEP LENGTH	6.307E+08	1.05117E+07	1.75194E+05	7299.8	19.986
STRESS PERIOD TIME	6.307E+08	1.05117E+07	1.75194E+05	7299.8	19.986
TOTAL TIME	6.307E+08	1.05117E+07	1.75194E+05	7299.8	19.986

APPENDIX-III

M T 3 D

A Modular Three-Dimensional Transport Model for Simulation of Advection, Dispersion and Chemical Reactions of Contaminants in Groundwater Systems

THE TRANSPORT MODEL CONSISTS OF 2 LAYER(S) 36 ROW(S) 46 COLUMN(S)

NUMBER OF STRESS PERIOD(S) IN SIMULATION = 1

UNIT FOR TIME IS T; UNIT FOR LENGTH IS L; UNIT FOR MASS IS M

<u>MAJOR TRANSPORT COMPONENTS TO BE SIMULATED:</u>

1 ADVECTION
2 DISPERSION
3 SINK AND SOURCE MIXING

NUMBER OF TIMES AT WHICH SIMULATION RESULTS ARE SAVED = 21

<u>TOTAL ELAPSED TIMES AT WHICH SIMULATION RESULTS ARE SAVED:</u>

0.0000 0.31540E+08 0.63070E+08 0.94610E+08 0.12610E+09
0.15770E+09 0.18920E+09 0.22080E+09 0.25230E+09 0.28380E+09
0.31540E+09 0.34690E+09 0.37840E+09 0.41000E+09 0.44150E+09
0.47300E+09 0.50460E+09 0.53610E+09 0.56760E+09 0.59920E+09
0.63070E+09

MAXIMUM LENGTH ALONG THE X (J) AXIS = 49340.00
MAXIMUM LENGTH ALONG THE Y (I) AXIS = 30660.00
MAXIMUM LENGTH ALONG THE Z (K) AXIS = 42.00000

<u>STRESS PERIOD NO. 001</u>

LENGTH OF CURRENT STRESS PERIOD = 0.6307000E+09
NUMBER OF TIME STEPS FOR CURRENT STRESS PERIOD = 1

```
TIME STEP MULTIPLIER =   1.000000
USER-SPECIFIED TRANSPORT STEPSIZE =   0.000000      T
MAXIMUM NUMBER OF TRANSPORT STEPS ALLOWED  IN ONE TIME
STEP =     50000

CONCENTRATION OF RECHARGE FLUXES WILL BE READ IN STRESS
PERIOD  1

NO    LAYER   ROW   COLUMN   CONCENTRATION      TYPE
  1         2        17           17           0.1000000E+09          WELL

                         TIME STEP NO.  001
FROM TIME =   0.0000     TO   0.63070E+09

MAXIMUM STEPSIZE DURING WHICH ANY PARTICLE CANNOT MOVE
MORE THAN ONE CELL
 = 0.2448E+08(WHEN MIN. R.F.=1)  AT K=   2, I=   1, J=  17

MAXIMUM STEPSIZE WHICH MEETS STABILITY CRITERION OF THE
ADVECTION TERM  (FOR PURE FINITE-DIFFERENCE OPTION, MIXELM=0)
 = 0.2444E+08(WHEN MIN. R.F.=1)  AT K=   2, I=   1, J=  17

 TOTAL NUMBER OF POINT SOURCES/SINKS PRESENT IN THE FLOW
MODEL =  3175

MAXIMUM STEPSIZE WHICH MEETS STABILITY CRITERION OF THE SINK
& SOURCE TERM
 = 0.7049E+08(WHEN MIN. R.F.=1)  AT K=   2, I=  20, J=  44

MAXIMUM STEPSIZE WHICH MEETS STABILITY CRITERION OF THE
DISPERSION TERM
 = 0.1946E+08(WHEN MIN. R.F.=1)  AT K=   2, I=   1, J=  16
```

TRANSPORT STEP NO.   1

```
TOTAL ELAPSED TIME SINCE BEGINNING OF SIMULATION = 0.000000
TOTAL PARTICLES USED IN THE CURRENT STEP =     20816
PARTICLES ADDED AT BEGINNING OF THE STEP =     20816
PARTICLES REMOVED AT END OF LAST STEP    =         0

CUMMULATIVE MASS BUDGETS AT END OF TRANSPORT STEP     1, TIME
STEP    1, STRESS PERIOD    1

                                  IN                    OUT
                            ----------------      ----------------
 CONSTANT CONCENTRATION:    0.000000              0.000000
          CONSTANT HEAD:    0.000000              0.000000
                  WELLS:    0.000000              0.000000
               RECHARGE:    0.000000              0.000000
     EVAPOTRANSPIRATION:    0.000000              0.000000
  MASS STORAGE (SOLUTE):    0.8314198E+08         -0.3396620E+08
              ----------------------------------------------------------------------
                [TOTAL]:   0.8314198E+08    M      -0.3396620E+08    M

         NET (IN - OUT):   0.4917577E+08
  DISCREPANCY (PERCENT):    83.98350
```

TRANSPORT STEP NO.   23

```
TOTAL ELAPSED TIME SINCE BEGINNING OF SIMULATION = 0.3469E+09 T
TOTAL PARTICLES USED IN THE CURRENT STEP =     50172
PARTICLES ADDED AT BEGINNING OF THE STEP =        96
PARTICLES REMOVED AT END OF LAST STEP    =       126
```

```
CUMMULATIVE MASS BUDGETS AT END OF TRANSPORT STEP   23, TIME
STEP    1, STRESS PERIOD    1

                                  IN                    OUT
                            ----------------      ----------------
CONSTANT CONCENTRATION:     0.000000              0.000000
         CONSTANT HEAD:     0.000000              0.000000
                 WELLS:     0.000000             -0.7127533E+10
              RECHARGE:     0.000000              0.000000
    EVAPOTRANSPIRATION:     0.000000              6841.693
 MASS STORAGE (SOLUTE):   0.9516485E+12          -0.3428298E+13
           -----------------------------------------------------------------------
               [TOTAL]:   0.9516485E+12    M     -0.3435425E+13    M

        NET (IN - OUT):  -0.2483777E+13
 DISCREPANCY (PERCENT):   -113.2316
```

TRANSPORT STEP NO.   41

```
TOTAL ELAPSED TIME SINCE BEGINNING OF SIMULATION = 0.6307E+09 T
TOTAL PARTICLES USED IN THE CURRENT STEP =     50362
PARTICLES ADDED AT BEGINNING OF THE STEP =       368
PARTICLES REMOVED AT END OF LAST STEP    =      190

CUMMULATIVE MASS BUDGETS AT END OF TRANSPORT STEP   41, TIME
STEP    1, STRESS PERIOD    1

                                  IN                    OUT
                            ----------------      ----------------
CONSTANT CONCENTRATION:     0.000000              0.000000
         CONSTANT HEAD:     0.000000              0.000000
                 WELLS:     0.000000             -0.1294939E+11
```

```
                    RECHARGE:    0.000000                 0.000000
         EVAPOTRANSPIRATION:    0.000000                 7216.990
     MASS STORAGE (SOLUTE):   0.5378841E+13            -0.6389180E+13
                ---------------------------------------------------------------------
                   [TOTAL]:   0.5378841E+13    M        -0.6402130E+13    M

             NET (IN - OUT):  -0.1023289E+13
    DISCREPANCY (PERCENT):   -17.37189
 -----
| M T |
| 3 D | End of Model Output
```