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In-situ observation and transport modelling of arsenic in Gangetic plain, India

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ABSTRACT

The focus of this study is to investigate the arsenic movement and impacts on the residual concentrations on groundwater pollution load. The Gangetic plain area in the Ballia, Uttar Pradesh is selected as study area, which is also reported to extreme arsenic pollution in soil-water system. A modelling approach is developed to assess the arsenic flux in partially saturated zone using data of soil texture, soil hydraulic properties and stratigraphy. Soil type, slope, and land-use cover is considered for estimating the transient flux at the top boundary from daily precipitation and evapotranspiration data of the study area. Solute transport in the subsurface is predicted by the mass transfer equation, which is derived by integrating Darcy's law with the equation of mass balance. The arsenic profiles of varying hydrogeological conditions associated with different locations in the study area are presented as breakthrough curves. The results shows that the arsenic transport is dominated by the advective flux and strongly depends on the soil-moisture flow conditions. Which may increases the arsenic load to underlaying groundwater resources. The simulated results suggest that mobility plays a vital role arsenic transport as well as on adsorbed arsenic concentration in subsurface. Likewise, the adsorption isotherms show that the high peak curve for Bairai and low at Sikarderpur. A higher pollution risk is observed in the Belthara Road, whereas a lower vulnerability is computed in the north and northeast regions. This study can help in strategising sustainable groundwater management and protection planning of identified regions of India.

1. Introduction

Arsenic pollution of drinking water is an issue of major concern. Due to its high toxicity to humans, the World Health Organization (WHO) has set a maximum concentration limit of 10 µg/L for arsenic in drinking water [1]. Soils are an aggregate-based structured media that have a multitude of pore domains resulting in varying degrees of advective and diffusive solute and gas transport [1]. Consequently, a spectrum of biogeochemical processes may function at the aggregate scale that collectively, and coupled with solute transport, determine element cycling in soils and sediments. A better understanding is needed to explore how the physical structure impacts biogeochemical processes influencing the fate and transport of As, and temporal changes in speciation and distribution of As through experimental measurement and reactive transport simulations.

Arsenic can exist in many organic and inorganic forms, depending on the origin sources and dominant reactions in soils [2]. Arsenic can form organic compounds by methylation as a biological process, producing both trivalent and pentavalent organo-arsenic compounds [3]. Environmentally significant arsenic compounds are arsenate and arsenite, because they are soluble in water and toxic. Distribution of arsenate and arsenite in the solution and solid phases is largely determined by adsorption and redox reactions in soils. Arsenic in sediments and soils is bound with solid phases at different strengths. The biogeochemistry of arsenic in heterogeneous soil systems is rather complex, comprising a large array of chemical and microbiological reactions, for example, adsorption–desorption, reduction–oxidation, dissolution–precipitation, acid–base reactions, and biomethylation [4]. Those

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reactions are affected by a series of environmental conditions such as pH, Eh, soil constituents, electrolytes, and microbial activity, temperature, and residence time. Traditionally, arsenic sorption studies have been carried out based on batch equilibration experiments conducted within a short period of reaction time.

The vulnerability assessment may be classified as the intrinsic and specific/integrated resource vulnerability. The intrinsic vulnerability depends solely on groundwater which is likely to the effected by imposed contaminant load. While, the specific/integrated vulnerability is determined for a particular pollutant or a certain prevailing human activity [5]. For resource vulnerability only unsaturated zone is considered whereas for source vulnerability, both the saturated and unsaturated zones are considered [6]. Groundwater contamination risk depends not only on vulnerability but also on the contaminant loading on ground surface for entering the subsurface environment [7].

The vulnerability assessment technique has been accepted for its competency to delineate the areas which are more likely, than others, to get contaminated as a result of anthropogenic activities at the surface. Another goal of vulnerability assessment is a subdivision of the area into several units which have different levels of pollution risk. Groundwater contamination can be minimized by delineating and monitoring vulnerable areas of the overlying watershed. Delineating surface areas which are responsible for groundwater contamination is a difficult task due to the involvement of many surface and subsurface parameters which play different roles in polluting groundwater resources. The general concept of groundwater vulnerability is based on the assumption that the physical environment may provide some degree of protection to groundwater against contaminant load making some land areas more vulnerable to groundwater contamination than others. Mostly hydro-geologic factors are used by the researchers for assessing groundwater susceptibility to contamination. These factors are often integrated into groundwater models using multiple methods for predicting susceptible surface areas responsible to groundwater pollution [8].

Assessment of groundwater vulnerability and pollution risk is used as important early tool in decision making and in management of groundwater resource [9]. It also provides a useful framework for effective implementation of contaminant protection programs and control measures [10]. The groundwater vulnerability maps assist to apprise and educate the people and create a general awareness about contamination problem of groundwater [6].

2. Objective

The main focus of this study is to assess the vulnerability and pollution risk of groundwater resources of Ballia District, which, in turn, could be incorporated into groundwater protection planning. The specific objectives are a). *In-situ* observation of arsenic contaminations, b). Lithological investigations, c). Batch scale laboratory experiments to investigate adsorption isotherms and, d) Numerical simulation of arsenic transport using field investigated data.

2.1. Study area

Ballia district, the eastern most part of the Uttar Pradesh lies between 25°23″ and 26°11″ North latitude and 83°38″ and 84°39″ East longitudes (Fig. 1). Total Geographical areas of the district is 2981 sq.km. District headquarter is at Ballia and there are six number of Tehsils namely Ballia (Sadar) Bansdih, Rasra, Belthra, Bairia and Sikanderpur. The district Ballia falls under sub humid climate with grassland vegetation. On the basis of climatic classification with PE index of 44.4. The temperature is maximum in May with 32.25 °C followed by June with 30.75 °C. The coldest month is December (12.15 °C) followed by January (15.9 °C). The humidity is maximum in August (82.5%) following by September (80%). Annual PET of Ballia district on the basis of Varanasi data is 1608.9 mm. The normal annual rainfall is 983 mm while monsoon rainfall is 864.8 mm. Ballia district is underlain by sands of various grades, gravels, silt and clay. These have wide extension. Arsenic above permissible limit in shallow aquifer is found in parts of Ballia district.

3. Materials and methods

The methodology follows the in-situ observation and transport modelling, a standard system for evaluating groundwater pollution risk. The coupled data based and physical pollutant transport modelling to contaminants of an aquifer based on their hydrogeological settings, are effective way to evaluates groundwater vulnerability.

3.1. In-situ observation

The in-situ observation plan was established at five different place of the study area. The sediment and groundwater samples were collected from all the selected locations. The groundwater samples were collected from the hand pump, in use of local communities. Furthermore, the sediment samples were collected from the depth of 25 cm at each location. All the samples were analysed in laboratory for Arsenic concentration as well as other physic-chemical parameters of collected groundwater and sediment samples.

3.2. Lithological investigations

The lithologs of each area was investigated by collecting the soil samples with different depth using core samples analysis. Required lithological data of the study area were obtained from the Central Ground Water Board (CGWB).

3.3. Batch experiments

In this study, a series of six batch sets containing 20 g of oven dried sand with particle size of 0.5–1.0 mm and 40% porosity were prepared under partially saturated condition. The detailed of soil types and texture is listed in Table 1. Various concentrations of Arsenic varying from 5 to 100 ppm were considered in the designed batches (Fig. 2). To maintain the level of saturation the 0.002L groundwater was added. The batch experiments were performed at room temperature (21.6 ± 0.3 °C) by maintaining the initial concentration. To prevent any other microbiological degradation, the effective concentration of $HgCl_2$ used for maintaining sterile conditions. The continuous hourly samples were analyzed using AAS to compute equilibrium break-through curve. To capture the high magnification at pore scale, SEM (Scanning Electron Microscopy) analysis was conducted at 10X.

3.4. Arsenic transport experiments

To investigate the fate and transport of toluene contaminated groundwater, a large scale column setup made of plexi-glass was fabricated. The column was 100 cm in length with an inner

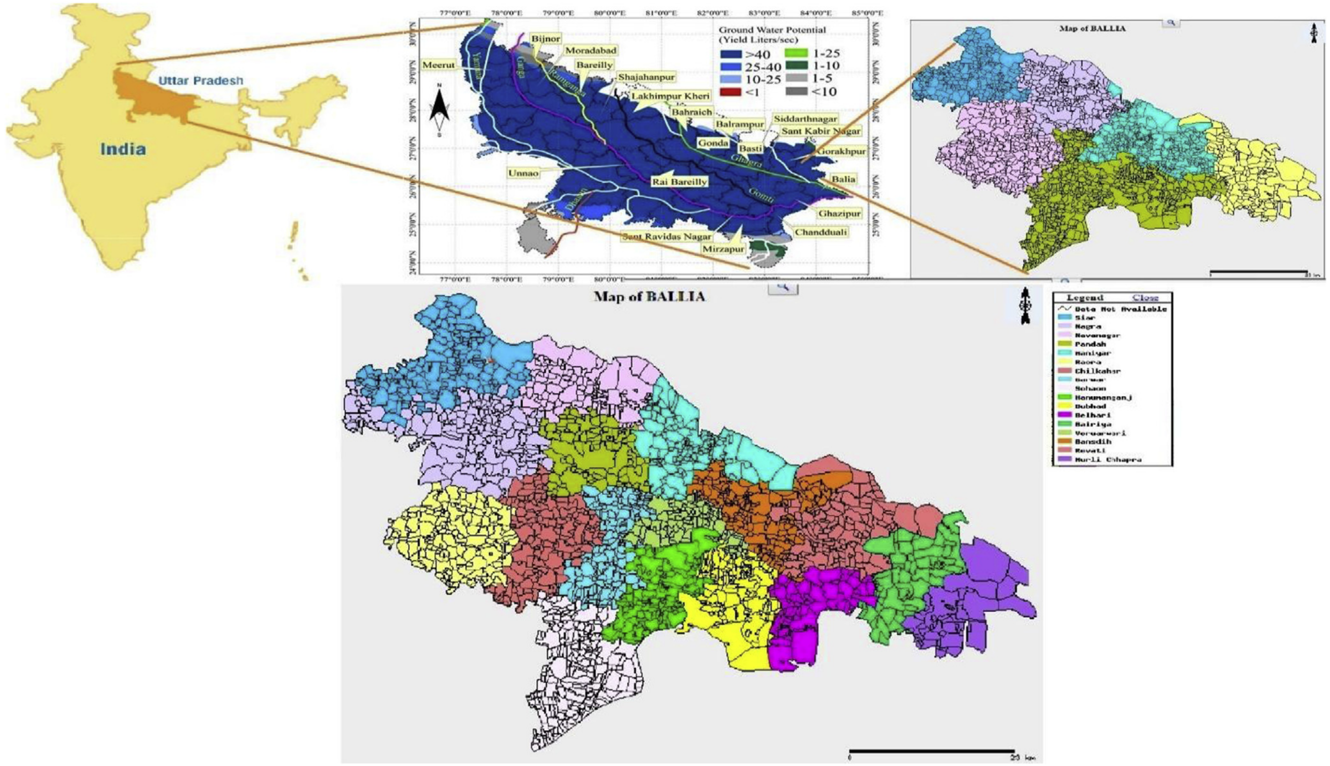

Fig. 1. The study area: Ballia District of Uttar Pradesh State, India.

Table 1
The properties of porous media used in batch experiment.

Porous media	Sand (g hg^{-1})	Silt (g hg^{-1})	pH	EC	OM	Bulk Density (g/cm^3)	Size	Types
Sand	92.8	4.2	5.5	4.9	0%	1.65	0.5–1 mm	Sand

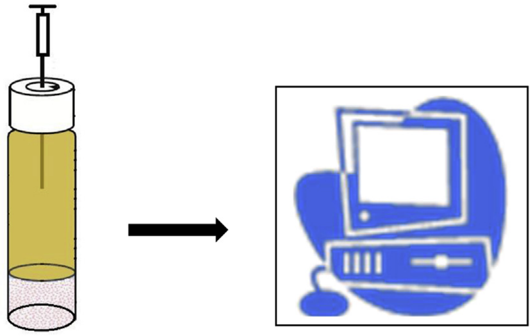

Fig. 2. The schematic diagram of batch experiment conducted to evaluate the fate of arsenic in soil-water system.

diameter of 12 cm. There were 5 sampling ports at a separation of 20 cm along length of the column. The column was packed homogeneously with saturated clean aquifer material collected from sites. The source of arsenic was prepared with oversaturated stock solution in millipore water. A continuous source of arsenic was mixed with groundwater coming from storage tank attached to the column by a peristaltic pump. A constant groundwater velocity of 0.625 cm/h was maintained in the vertical direction throughout the experiment. A free drainage was allowed at the bottom and a constant hydraulic head of 2.0 cm was maintained at the top throughout the period of the experiments in both the cases. The schematic diagram of these experimental sets is shown Fig. 3.

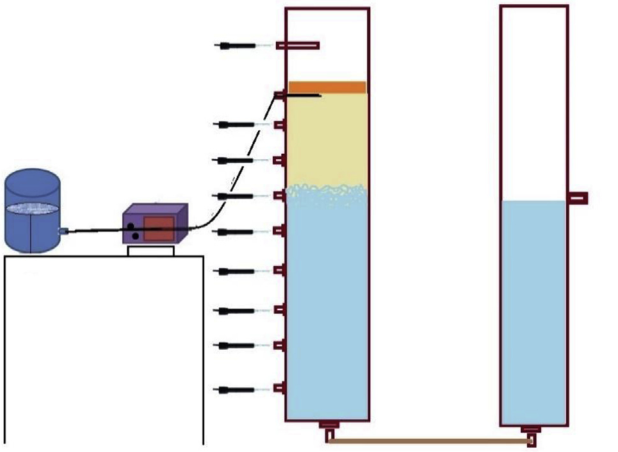

Fig. 3. Schematic diagram of the column set-up for investigating arsenic transport in groundwater zone.

3.5. Governing equations and numerical simulation

The solute transport in a one-dimensional homogeneous porous medium under steady state uniform flow conditions; for conservative nature and if sorption occurs under local equilibrium conditions [11]; is governed by:

$$D_x\frac{\partial^2 c}{\partial x^2}+D_y\frac{\partial^2 c(t,x,y)}{\partial y^2}-V_x\frac{\partial c(t,x,y)}{\partial x}=R_f\frac{\partial c(t,x,y)}{\partial t}$$

Where V_x is the average unidirectional interstitial ground water velocity; Rf is the dimensionless retardation factor; and D_x, D_y, and D_z are the longitudinal, transverse, and vertical hydrodynamic dispersion coefficients, respectively.

The HYDRUS is graphical user interface tool coded on above mention governing equation of the variably saturated subsurface water flow and solute transport [12]. The simulation projects were created in 1D general types of geometry having vertical plane XZ (Fig. 4). The van-Genuchten-Mualem single porosity model was selected for the domain. The van-Genuchten parameters were used as material properties of the water flow for single sand media showed in Table 1. The space discretization followed the Galerkin finite elements approaches and time discretization followed Crank-Nicholson scheme for the solute transport [13]. Finally, the mass balances were calculated for the study domain.

The conditions outside the domain of our interest can influence what is going on inside the domain. For solving steady state equations of groundwater flow only boundary conditions need to be specified [14]. In this simulation, the top boundary condition was applied as constant flow and remains were no flux boundary conditions. However, for solving unsteady flow equations, initial condition also has to be specified. The initial condition provides the hydraulic head everywhere within the domain of interest before the simulation begins (i.e., at $t = 0$). The initial conditions are expressed as $h(x,y,z,0) = h_0(x,y,z)$ Where, h_o is the initial hydraulic head in the domain considered.

3.6. Arsenic risk map

Human activity on land surface has greater influence on groundwater quality and characterises the pollution risk of the target area. Land use map of the study area is classified into four land use/land cover classes: 1) forest, 2) agriculture, 3) water bodies, and 4) settlement. The pollution risk map is generated by incorporating the land use of the area as top boundary conditions. Which results on the more realistic outcomes of Arsenic transport in subsurface. Finally, a risk map was prepared using the outcomes of data based analysis and solute transport modelling techniques.

4. Results and discussion

4.1. Meteorological event analysis

Using the above mentioned methodological framework with integration of different approaches and methods, the quantitative vulnerability mapping comes in figure for the entire study area. The results of all five station of study area, were estimated runoff and recharge on the monthly and seasonal basis. Monthly basis is estimated by separated month's results and seasons are of three basis, Pre-Monsoon i.e. February to May, Monsoon Season i.e. June to September, and Post-Monsoon, i.e. Octobers to January. Table 2 showed the estimated values of the water balance components of the study area. The study showed the total 92% of rainfall occurs in 4 month of monsoon season i.e. June to September whereas out of them 70% rainfall is flowing as runoff and only 4.7% of rainfall is infiltrated as recharge in soil-water system during the monsoon season.

4.2. In-situ quality observation

The in-situ observation plan was established to collect initial concentration data at five different place of the study area. The sediment and groundwater samples were collected from all the selected locations. The groundwater samples were analysed and the results tabulated in Tables 3 and 4. The qualitative assessment of collected groundwater samples gives the hydro-chemical variables considering the parameters, which affect the water chemistry

Table 2
Estimated water balance components and the net recharge volume of the entire study area.

Water Balance Components	Values
Rainfall [mm]	624.3
Runoff [mm]	454.2
Recharge [mm]	30.6
Runoff coefficient	0.6
Recharge Coefficient	0.04

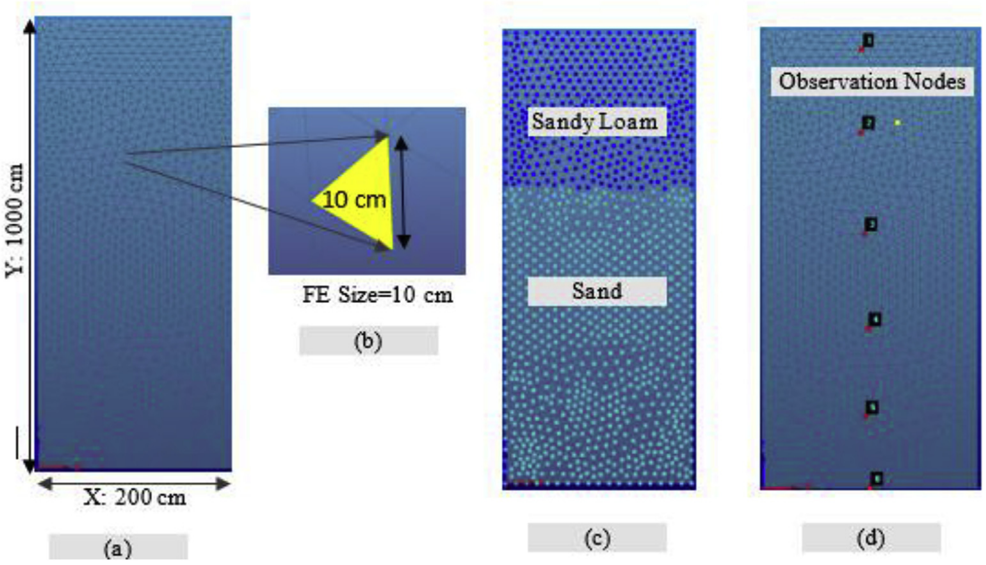

Fig. 4. Representing the properties of simulation domain, (a) elemental geometry, (b) FE Size, (c) material distribution, (d) observation nodes.

Table 3
The analysed values of the pH, EC, Salinity, Alkalinity, Sodium and Potassium for collected groundwater in study area.

S.N.	Sampling Site	pH (Standard Value 6.5–9.2)	EC (0–800 uS/cm)	Salinity (200–600 mg/L)	Alkalinity (10–500 mg/L)	Hardness (300)	Electrolyte Na^+(ppm) (300 ppm)	Electrolytes K^+ (300 ppm)
1	Bairai	8.3	420	455	95	296	**480**^	300
2	Ballia	7.2	480	**755***	125	295	450	948
3	Rasra	6.8	485	320	185	310.5	420	**1210****
4	Belthara Road	7.1	485	480	95	302	246	370
5	Sikarderpur	6.9	520	512	112	**305**#	268	420

*Highest value of salinity in rural area of ballia, #High hardness value in Sikarderpur; ^High Na^+ value in Bairai; and ** Very high K^+ vale in Rasra.

Table 4
The analysed values of the total Arsenic in groundwater and sediment of study area.

Sampling Site	Total As in Groundwater (μg/L)	Total As in Sediments (μg/L)
Bairai	80.3	20
Ballia	75.2	18.5
Rasra	65.8	16.5
Belthara Road	70.1	18
Sikarderpur	116.9	25

and change the water quality. The qualitative assessment is equally important for the vulnerability mapping at any regional study and planning. The bold mark data show the extreme values of the hydro-chemical variable. The comparative mark is done with the respect to Indian standards of water qualities for drinking water standards. The results show the satisfactory statues of pH, EC and Alkalinity of all study sites. The extreme maximum values for salinity is about 755 mg/L in ballia sites and minimum values is about 320 mg/L at Rasra sites, which is unacceptable values to drinking water standard. Out of 05 sampling site, 03 sites have extreme maximum values of hardness and Na.

Arsenic concentration in 5 samples of Ballia district varied from 70 to 116 μg/L. Concentration higher than 116 μg/L were observed in Sikarderpur and lesser in Bairai (80 μg/L). All the sites having higher As concentration in groundwater and sediments as WHO and BIS standard of 10 μg/L. The Arsenic concentration is also due to the natural weathering of racks but high concentration show the over-exploitation of groundwater in the representative area and sites of sampling. The Quality assessment gives the strong background study for the policy, plan of action for sustainable water resources management in study area. Fig. 5 shows the observed Arsenic concentration in collected groundwater samples and sediments.

4.3. As adsorption isotherms

The two most common models to describe adsorption process are the two-parameter isotherms of Langmuir and Freundlich. The Langmuir adsorption isotherm can be described by the equation-

$$Q_{ad} = Q_{sat}\frac{K_{ad}C_{eq}}{1 + K_{ad}C_{eq}}$$

Where Q_{ad} is the specific adsorbed quantity of a model compound and C_{eq} is the pollutant concentration, both at equilibrium; Q_{sat} is the saturation (maximum) adsorption capacity and K_{ad} is the adsorption constant. The computed and observed isotherm is presented for all location in Fig. 6.

4.4. Arsenic transport

By applying different water flow and arsenic transport boundary condition and considering single porosity approach, the subsurface domain was simulated using iteration techniques. The simulated results suggest that mobility plays a vital role both in cumulative arsenic transport as well as in sorbed arsenic concentration in deep zone. Fig. 7 shows the arsenic transport profile in vertical domain at 1hr, 6hr, 12hr, 24hr. The resulst shows that the arsenic transport is dominated by the advective flux and strongly depends on the soil-moisture flow.

Results of numerical simulations show that these physical processes significantly affect the arsenic transport profiles of different locations. Further, their reduced species, and arsenate as well as arsenite that will result from the degradation of an organic carbon source in the sediments or groundwater. Even though specific biological transformations are allowed to proceed only in zones where they are thermodynamically favourable, results show that mixing as well as abiotic reactions can make the profiles of individual electron acceptors overlap and/or appear to reverse their expected order.

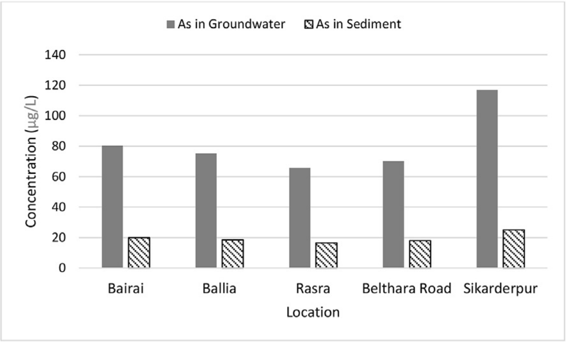

Fig. 5. The analysed values of the total Arsenic in groundwater and Sediment samples collected from five different locations in Ballia district.

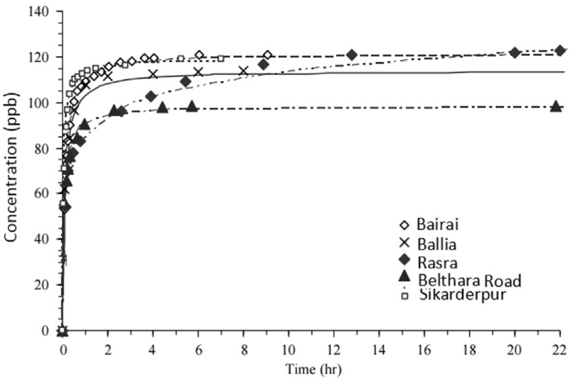

Fig. 6. Adsorption Isotherms measured using batch experiment for all five sites.

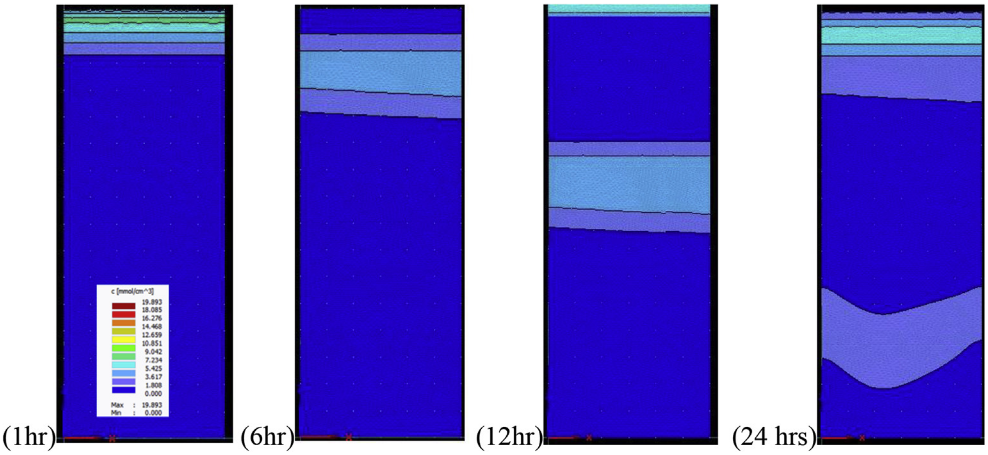

Fig. 7. The Arsenic transport profile in vertical domain at 1hr, 6hr, 12hr, 24hr. The alternate color lines shows the arsenic regims in subsurface.

5. Conclusion

In this study, arsenic transport modeling using in-situ observed data was incorporated to indicate the groundwater vulnerability of the study area. The hydrogeological setting, land use pattern, soil types of the study area was applied for vulnerability assessment of shallow groundwater resources under steady-state and transient boundary conditions. The simulated travel time required by the solute peak to reach the water table is used for computing the vulnerability index for the entire study area. A higher pollution risk is observed in the Belthara Road, whereas a lower vulnerability is computed in the north and northeast regions. This study can help in strategy making for groundwater management and protection planning. Macroscale heterogeneity, especially the fracture porosity, can be incorporated for improving the simulations of flow and transport regimes [15]. Further, a nonconservative type of solute can also be considered to take into account the geochemical processes of the subsurface.

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