Numerical Modelling of Benzene Biodegradation in Aquifers Under the Presence of Multiple Electron Acceptors

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Abstract. The influx of petroleum hydrocarbon into the aquifers due to piping leaks, an accidental spill of petroleum products, and leakage from underground fuel tanks at diesel and petrol pumps are some of the leading causes of aquifer pollution. This study presents a numerical model for subsurface investigation of benzene biodegradation in aquifers. Among the four BTEX (benzene, toluene, xylene, ethylbenzene) compounds, benzene is the most difficult to undergo degradation. This is because benzene has the highest C–H bond dissociation energy (473 kJ mol $^{-1}$) among all the hydrocarbons. A fully implicit finite-difference approach is adopted here to analyse and solve the proposed numerical model, which is capable of obtaining the spatial variation in benzene concentrations. It is observed from the conducted research that biodegradation effectively limits the transport of benzene in aquifers. The investigation, in addition, can help in deducing the optimum rate at which electron acceptors are injected into the aquifer and the time required to reduce the concentration of benzene to desirable limits. The model also generates the scope of being used as a predicting tool for monitoring the efficacy of different biodegradation enhancement strategies in aquifers**.**

Keywords: Biodegradation, Benzene, Numerical modeling.

1. Introduction

Aromatic hydrocarbons like benzene, toluene, ethylbenzene and xylene (BTEX) are the primary components of petroleum products. These substances are frequently found in soil and groundwater due to leaks from pipelines and underground storage tanks, unintentional spills at production spots, and accidents during transportation. Because of its high aqueous mobility and solubility, which allow it to move through aquifers, BTEX generally have large scale effects on the aquifer environment [1]. Pollution caused by BTEX becomes detrimental when the adjacent aquifer is used as a source of drinking water. BTEX constituents are not only toxic but also cause undesirable odour. When petroleum is spilled into the aquifer, it passes through many mechanisms that alter the structure and the concentration of the hydrocarbon.

The amount of benzene in petroleum is usually less than 2%, but it plays a crucial role because it is the most hazardous and chronic component among the family of hydrocarbons [2]. The solubility of benzene in water is only 1.78 g [4], yet it is the most soluble among petroleum hydrocarbons. Natural attenuation results in the decomposition of toluene, ethylbenzene, and xylene in aquifers but for benzene, this process is slow [3]. The complex chemical structure of benzene makes it more difficult to break down. Low molecular weight aromatic benzene has relatively higher water solubility [5]. It can indeed be utilized as a tracer of crude oil spills as it has high water–air partitioning coefficient and higher solubility [6]. Since benzene is perhaps the most poisonous mono-aromatic hydrocarbon, its occurrence in areas where gasoline has been contaminated often indicates the requirement for remedial intervention [7]. The toxicity and stability of contamination are strongly influenced by these physico-chemical and biological mechanisms [8].

Benzene components can be treated mainly by biodegradation in oil spill locations. Therefore, it is necessary to understand how benzene changes during its transport through the subsoil. Hydrocarbons act as an electron donor during the biodegradation process. Oxygen (O_2), nitrate (NO^{3-}), sulphate (SO_4^{2-}), ferric ions (Fe (III)), and carbon dioxide are some of the electron acceptors. The redox reaction between electron donor and electron acceptors releases energy that bacteria can use for its growth. A large number of lab and field studies were analysed and compared. Various published investigations failed to validate anaerobic benzene breakdown. Some of them actually showed that degradation of benzene was under nitrate, manganese-reducing, and occasionally methanogenic environments. In their study of BTEX cleanup from groundwater in the presence of electron acceptors, [2, 9] found that benzene was the most resistant substance. Toluene, Ethylbenzene, and a-xylene were eliminated within less than 10 days of nitrate reduction. After 60 days, toluene and xylenes were eliminated in the presence of sulphate. Anaerobic bacteria can decompose BTEX under the presence of different electron acceptors, such as nitrate Fe^{3+}, sulphate and manganese, according to field and laboratory micro investigations [7]. Understanding the genetic and molecular origins of benzene biodegradation has made big progress. To address the various mechanisms involved in benzene fate and transit, multiple numerical models were applied. The MODFLOW model from the U.S. Geological Survey was used to determine groundwater flow velocities based on domain parameters hydraulic gradient, soil porosity, and hydraulic conductivity [10].

However, literature lags in numerical modeling for variations in the capability to degrade benzene under the presence of different electron acceptors and microbes sequentially. Therefore, fundamental knowledge of the various interconnections between benzene degradation at different rates and the effectiveness of various substrates for in-situ clean-up in polluted areas must be established. In order to study pollutant transport and fate, numerical simulation is frequently employed as a good supplement due to the limitations of field studies and the lack of experimental data. [11].

Following previous research, we looked further in this work how benzene degrades when exposed to oxygen and nitrate, two distinct electron acceptors sequentially. In the present study, a two-dimensional numerical modelling investigation is performed to show that benzene could be degraded under strictly anaerobic conditions. Model validation is sought through comparisons of model predictions in previous studies. The main objective of the research described in this work is to simulate transport, fate, and complex biodegradation processes, of benzene in presence of two electron acceptors and microbes using a sequential reactive transport numerical model.

2. Mathematical Equations for multispecies transport

A multicomponent transport model is developed to investigate benzene migration in the aquifer in the presence of two electron acceptors and microbes. The groundwater aquifer is assumed to be homogenous and isotropic for this modeling study. It is also assumed that groundwater flow is uniform. Equation 1 can be used to depict the transient transport of benzene (electron donor) within the ground water aquifer. Equation 2 and 3 represents the transport model for electron acceptors and microbes, respectively.

$$R_i \frac{\partial C_i}{\partial t} = D_{i,x} \frac{\partial^2 C_i}{\partial x^2} + D_{i,z} \frac{\partial^2 C_i}{\partial Z^2} - V_{i,x} \frac{\partial C_i}{\partial x} - V_{i,z} \frac{\partial C_i}{\partial z} - R^b_{bio} \, C_i \qquad (1)$$

$$\frac{\partial (C_o)}{\partial t} = D_{ox} \frac{\partial^2 C_o}{\partial x^2} + D_{oz} \frac{\partial^2 C_o}{\partial Z^2} - V_{o,x} \frac{\partial C_o}{\partial x} - V_{o,z} \frac{\partial C_o}{\partial Z} - R^o_{bio} \, C_o \qquad (2)$$

$$\frac{\partial (C_m)}{\partial t} = D_{mx} \frac{\partial^2 C_m}{\partial x^2} + D_{mz} \frac{\partial^2 C_m}{\partial Z^2} - V_{n,x} \frac{\partial C_m}{\partial x} - V_{m,z} \frac{\partial C_m}{\partial Z} - R^m_{bio} C_m \qquad (3)$$

In Equations 1- 3 C_i, C_0, C_m represents the concentration of benzene, electron acceptors, and microbes, respectively [ML^{-3}]; V_x represents the groundwater flow velocity in x direction [LT^{-1}]; V_y represents the groundwater flow velocity in the y direction [LT-1]; R_i represents the retardation factor [-]; $D_{i,x}$ is the dispersion coefficient along the x direction [L^{2}T^{-1}]; $D_{i,y}$ is the dispersion coefficient along the y direction [L^{2}T^{-1}];

The first and second components of Eqn. (1-3) on the R.H.S represents the dispersion of dissolved benzene, electron acceptors, and microbes within the groundwater aquifer in the x and y-direction, respectively. The third and fourth terms of Eqn. (1-3) on the R.H.S represents the advection of the dissolved benzene, electron acceptors, and microbes in x and y-direction.

The dispersion coefficients of dissolved benzene components along x and y directions can be described as provided in Eqn. (4) & (5).

$$D_{i,x} = a_x V_x + D_i^*$$ (4)

$$D_{i,y} = a_y V_y + D_i^*$$ (5)

In Eqn. (4), a_x is the dispersivity along the x direction [L] and D_i^* is the molecular diffusion coefficient of ith benzene component [$L^2 T^{-1}$]. In Eqn. (5), a_y is dispersivity in the y direction [L].

This modelling considers biodegradation occurring sequentially in the aquifer. Rate of biodegradation for microbes, electron acceptors and benzene is simulated using Monod kinetics in the present modelling.

R^b_{bio}, R^o_{bio}, R^m_{bio} are the biodegradation rate of benzene, electron acceptors, and microbes [T^{-1}]. Expressions governing biodegradation rates are provided in Eqns 6-8

$$R^b_{bio} = M_{sus} \mu_{max,i} \cdot \frac{C_i}{Ks_i + C_i} \cdot \frac{1}{Ks_o + C_o}$$ (6)

$$R^o_{bio} = M_{sus} \mu_{max,i} \cdot sto_i \frac{C_i}{Ks_i + C_i} \cdot \frac{1}{Ks_o + C_o}$$ (7)

$$R^m_{bio} = \theta \cdot M_{sus} \mu_{max,i} \cdot \frac{C_i}{Ks_i + C_i} \cdot \frac{1}{Ks_o + C_o}$$ (8)

$\mu_{max,i}$ is maximum substrate utilization of benzene [T^{-1}]; Ks_i represents the half-saturation constant of electron donor [ML^{-3}], Ks_o represents the half-saturation constant of electron acceptors [ML^{-3}], and sto_i is the stoichiometric constant of biodegradation reaction [–]. M_{sus} is the microbial concentration [ML^{-3}].

3. Numerical modeling

To develop a model of the transport equation for dissolved benzene in an aquifer, the above equations are solved in every time step. Five sequential models are simulated in present study for one electron donor, two electron acceptors and two microbes. This modelling study is performed using operator splitting method. Advection and dispersion term is solved using finite difference scheme. Biodegradation term is solved with the help of Runge Kutta approach. A time-varying boundary condition can be used to accommodate the benzene's transient dissolving rate. The transport of contaminants throughout the aquifer in Eqs. (1)–(8) are solved taking into account the boundary conditions of the benzene, electron acceptors, and microbe model.

Expression for the initial conditions of various components is provided in Eqn. (9-11).

$$C_i(x, z, t = 0) = C_{ini} \tag{9}$$

$$C_o(x, z, t = 0) = 5 \text{ mg/l} \tag{10}$$

$$C_m(x, z, t = 0) = 0.5 \text{ mg/l} \tag{11}$$

The model includes dissolution from the source zone by incorporating time-varying boundary constraints for benzene components at the source zone. The length of the source zone is $(s_2 - s_1)$. The boundary condition for dissolved benzene components near the source zone is provided in Eqn. (12). No flux boundary condition is adopted at all other boundaries except the source zone. Schematic view of computational domain corresponding to physical system adopted in this study is shown in Fig. 1

$$C_i(x > s_1 \& x < s_2, z = 0, t) = C_{S,i}(t) \tag{12}$$
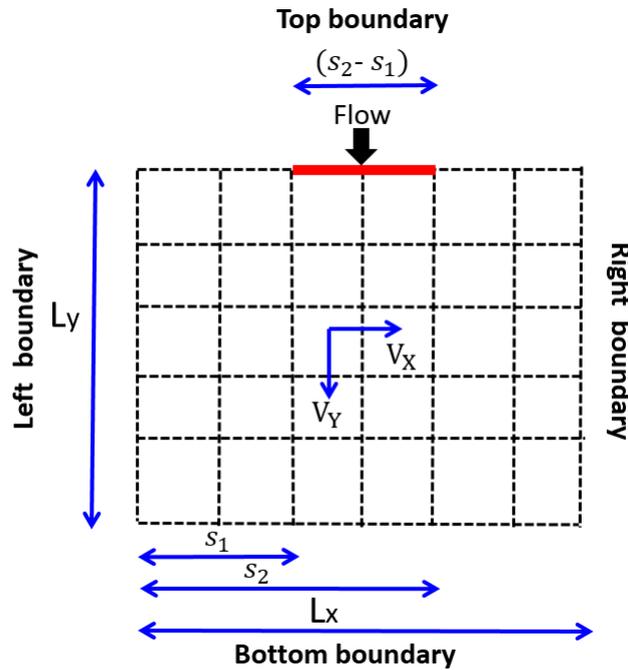
Fig. 1 Schematic view of computational domain corresponding to physical system

4. Results and discussion

Table 1 Parameters adopted in the simulation process

Parameter	Units	Benzene	Reference
Initial solubility	(mg/l)	1780	
Yield	-	0.5	
Half saturation constant	(mg/l)	2	[12]
Molecular weight	(g/mol)	78	
Stoichiometric mass ratio	-	3.08	
Maximum sub-strate utilization rate	(day^{-1})	0.5	
Free molecular diffusion coefficient	(m^2/day)	10^{-5}	[13]
Retardation factor	(-)	1.34	[14]
Initial number of moles	(-)	1	Assumed

Fig. 2 represents the spatial distribution of dissolved benzene in a groundwater aquifer without biodegradation. Fig. 3 represents the spatial distribution of dissolved benzene in a groundwater aquifer under the presence of two electron acceptors and microorganisms through a contour map. Table 1 enlists the input parameter adopted for this simulation study. The contour profile shown is generated after a simulation period of 50 days. The source zone for benzene is assumed to be at the top boundary. The migration depth for dissolved benzene concentration is more than 1 cm in the vertical direction in case of migration of benzene without biodegradation. It is observed from the figure 2-3 that benzene plume length is decreased as it migrates vertically downward from its source zone in fig. 3 when compared with fig. 2. It is due to the presence of electron acceptors and microbes inside the aquifer that can cause a substantial reduction in the concentration of benzene with depth. The decline in benzene concentration in the presence of electron acceptors and microbes is because of the biodegradation of benzene in the groundwater aquifer.
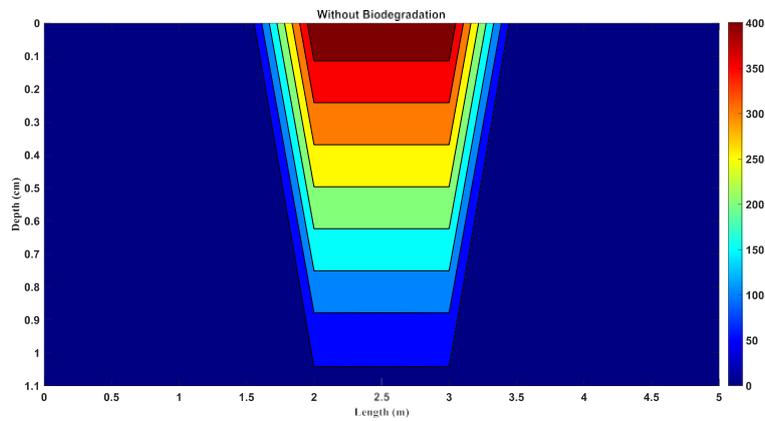
Fig. 2 Spatial distribution of benzene for 50 days simulation period
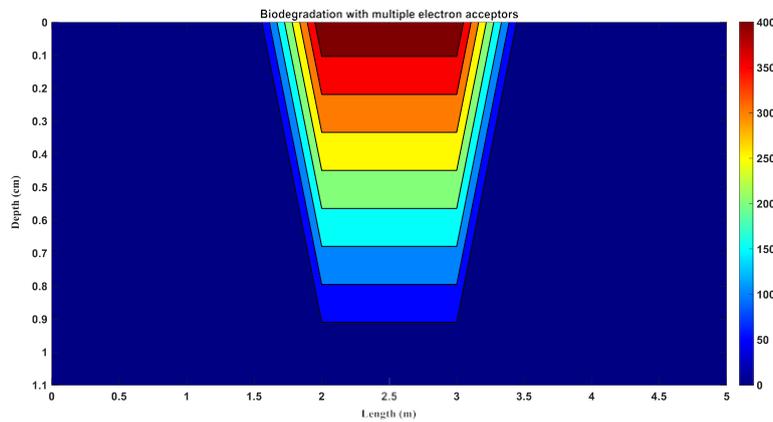
Fig. 3 Spatial distribution of benzene for 50 days simulation period

Cell respiration is the method by which cells gain the energy required for their metabolic functions which involves a series of redox reactions in which energy is collected by sequential oxidation by removing electrons. At each step, a relatively higher oxidised substance must be present in order to progress and avoid an electron assemblage that would slow down the reaction's kinetics. That substance described as electron acceptors act as a "sink" for the electrons generated. Dissolved benzene concentration is more in the area of oil spill, but the concentration of electron acceptors shows an opposite behavior. Fig. 4-5 gives the concentration profile of electron acceptors in the aquifer system. The inlet concentration of both the electron acceptors i.e. dissolved oxygen and nitrate is considered to be 5 mg/l. From fig 4 it can be seen that the dissolved oxygen concentration is reduced in the area where benzene concentration is high. This is due to the biodegradation of dissolved benzene, which consumes some dissolved oxy-

gen. Once the dissolved benzene is degraded amount of benzene will reduce, and dissolved oxygen will return to its original concentration. After 7 cm depth concentration of dissolved oxygen comes to its original mass. Dissolved nitrate concentration also shows a similar trend, however, with less reduction in the concentration because the present model considers biodegradation reaction by electron acceptors is occurring sequentially. Also, it attains its initial concentration after 6 cm depth of migration as shown in fig. 5.
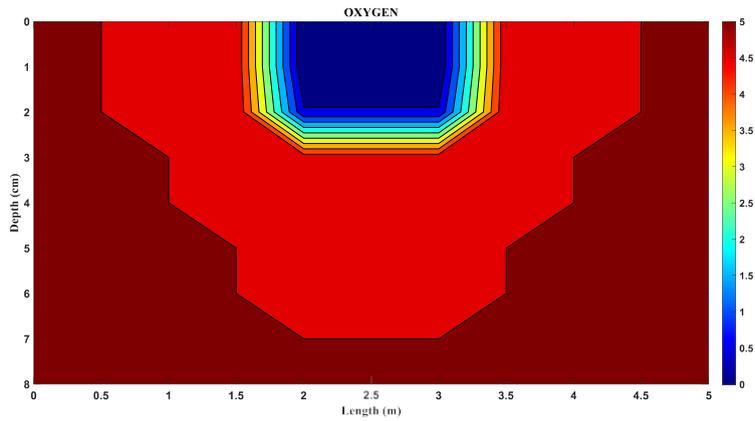
Fig. 4 Spatial distribution of dissolved oxygen for 50 days simulation period
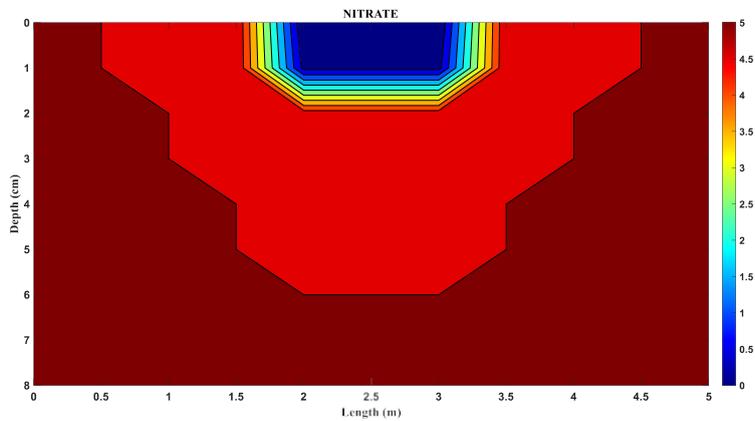
Fig. 5 Spatial distribution of nitrate for 50 days simulation period

Benzene attenuation due to microbial degradation has a critical role in benzene fate in the aquifer. Bacteria uses the energy released during the reaction between electron donor and electron acceptor for its growth. Fig 6-7 shows the concentration distribution of bacteria for a simulation period of 50 days. Microbial activity will be predominant

at the site of the spill, where advective fluxes of nitrate and oxygen occur because of enhanced benzene concentration. Microbial concentration will be more at the place where the contaminant is more but, outside the plume there is no bacterial growth. Both denitrifying and aerobic bacteria show almost similar trend. Since the decay constant of microbes is assumed as zero, therefore the cumulative microbes will increase in the system.
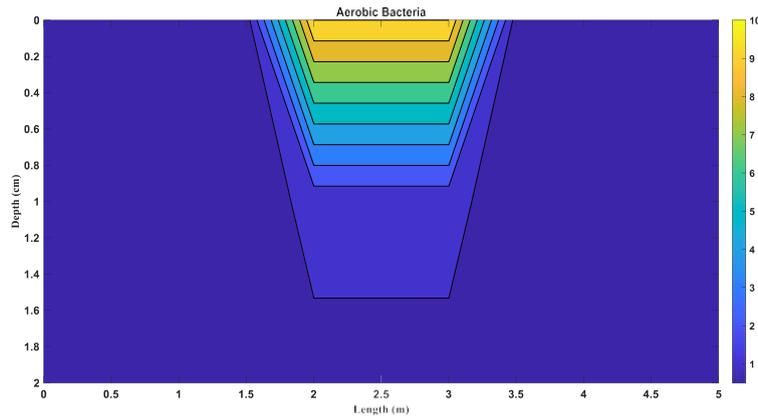
Fig 6 Spatial distribution of aerobic bacteria for 50 days simulation period
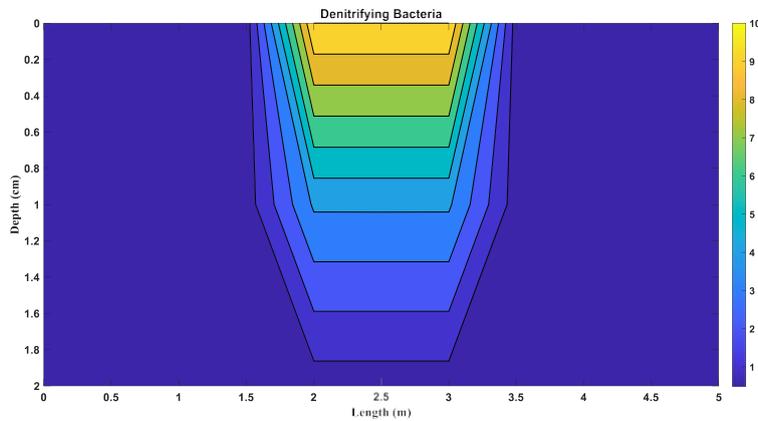
Fig 7 Spatial distribution of denitrifying bacteria for 50 days simulation period

5. Conclusion

Biodegradation resulted in the reduction in plume length of dissolved benzene in the aquifer. In the present modelling study it is found that consumption of dissolved oxygen is more than nitrate in the degradation process because process of biodegradation is considered to occur sequentially in the system. Micro-organism concentration will be more in the area where contaminant is more because microbes uses benzene as the source of food for their cell growth.

This model can be further used in planning remediation strategies for aquifer contaminated by petroleum hydrocarbons using bio-stimulation, bio-augmentation or other in-situ bio-attenuation techniques. This information can be used to provide an idea about the rate of injection for electron acceptors, the timescale of injection, and the time - period needed to reduce contaminant concentration in the aquifer system. One can also use this predictive modelling in developing an optimization tool for bioremediation of contaminated aquifers.

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