

# An Assessment of Factors Affecting Reactive Transport of Biodegradable BTEX in an Unconfined Aquifer System, Tehran Oil Refinery, Iran

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## Abstract

Risk-based assessment methods are commonly used at the contaminated sites by hydrocarbon pollutants. This paper presents the results of a two-dimensional finite volume model of reactive transport of biodegradable BTEX which have been developed for the saturated zone of an unconfined aquifer in the Pump station area of Tehran oil refinery, Iran. The model governing equations were numerically solved by modification of a general commercial software called PHOENICS. To reduce costs in general, many input parameters of a model are often approximated based on the used values in the contaminated sites with same conditions. It was not fully recognised the effect of errors in these inputs on modelling outputs. Thus, a sensitivity analysis was carried out to determine the influence of parameters variability on the results of model. For this analysis, the sensitivity of the model to changes in the dispersivity, distribution coefficient, parameters of Monod, Michaelis-Menten, first- and zero- order kinetics modes on the BTEX contaminant plume were examined by performing several simulations. It was found that the model is sensitive to changes in dispersivity and parameters of Michaelis-Menten, first- and zero- order kinetics model. On the other hand, the predictions for plumes assuming Monod kinetics are similar, even if different values for parameterization are chosen. The reason for this insensibility is that degradation is not limited by microbial kinetics in the simulation, but by dispersive mixing. Quantifying the effect of changes in model input parameters on the modelling results is essential when it is desired to recognise which model parameters are more vital on the fate and transport of reactive pollutants. Furthermore, this process can provide an insight into understanding pollutant transportation mechanisms.

**Keywords:** Rey Industrial Area, finite volume model, BTEX, biodegradation, sensitivity analysis, kinetics models

## 1-Introduction

Oil refining operation around the Rey Industrial Area, south of Tehran, Iran has resulted many environmental hazards including soil and groundwater pollution by BTEX compound (benzene, toluene, ethylbenzene, xylene) (Fusione Techno Solutions Co., 2006). It has been investigated that groundwater pollution is most serious.

One of the main features in the simulation of fate and transport of BTEX in the saturation zone of an unconfined aquifer is to consider the variability of the model predictions by changing the values of the modelling parameters. According to Davis (1983), a sensitivity analysis provides necessary information for understanding

which model parameters better manage modelling predictions.

This paper considers the sensitivity of the model to changes in the dispersivity, distribution coefficient, parameters of Monod, Michaelis-Menten, first- and zero-order kinetics models on the contaminant plume. Several runs were performed to simulate the reactive transport of BTEX through an unconfined aquifer system in the Pump station area of Tehran oil refinery, Iran.

For performing this sensitivity analysis a numerical finite volume model has been developed by the modification of a general commercial package called PHOENICS (Spalding, 1981). The necessary coding for

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mathematical expressions relating to the chemical and biological reactions was written in the FORTRAN 99 language and was supplied in PHOENICS user-accessible subroutine called GROUND (Doulati Ardejani et al., 2004 a, b). These FORTRAN codings for all non-standard computations were used by PHOENICS solver during the course of the solution process.

## 2-Site description and environmental impacts

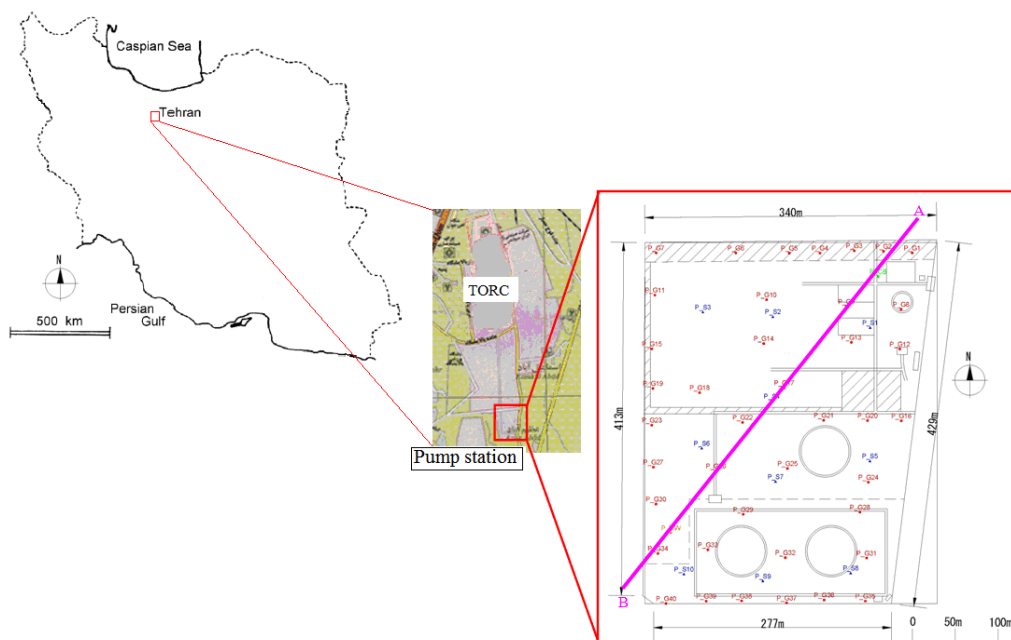
The investigation area is located in the Pump station in the south side of Tehran Oil Refinery (TOR), south of Tehran, Iran (Figure 1). Groundwater and soil pollution by oil containing BTEX compound has been investigated around the Rey industrial area since 1970's.

A detailed environmental study has been carried out to locate the main sources of pollutant release. In addition, some site remediation strategies and controlling plans have been proposed (Fusione Techno Solutions Co., 2006). The focus was mainly on bioremediation method.

However, BTEX plume is expanding in the site year by year.

At this stage, exact determination of contaminant BTEX plume can provide useful information to develop an appropriate site remediation plan to control further groundwater pollution problem in the study area.

Numerical models are extensively used for simulation of contaminant transport through groundwater flow systems. Numerical models can help to design, optimise and predict performance of field remediation strategies. Such models can be used as a useful tool to determine BTEX plume more accurately. Hence, in response to the request, financial and technical supports by the Tehran oil refining company, the authors have developed a numerical finite volume model to simulate BTEX fate and transport through the groundwater flow system; taking physical, chemical and biological processes into account. The present research only considers the sensitivity of the model to changes in the model input parameters on model predictions for BTEX plume.

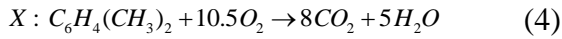
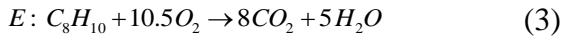
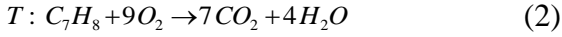
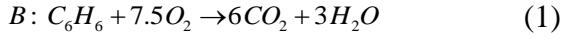


**Figure 1. Geographical situation of the Tehran Oil Refining Company and investigation area in details (Modified from Fusione Techno Solutions Co., 2006).**

### 3-Model development/ Governing equations

#### 3-1-Oxygen-limited biodegradation

The chemical reactions describing BTEX oxidation can be given as follows (modified from Anid et al. 1993, Agah et al., 2011):



#### 3-2-Bacterial models

##### 3-2-1-Monod kinetics

Taking Reaction 1 into consideration, the Monod kinetics expressions describing oxygen limited biodegradation of BTEX and oxygen consumption are given as (Schafer et al., 2005; Cirpka and Valocchi, 2007):

$$R_{BTEX} = \frac{\partial C_{BTEX}}{\partial t} = -\frac{C_{BTEX}}{K_{BTEX} + C_{BTEX}} \frac{C_{O_2}}{K_{O_2} + C_{O_2}} \frac{\mu_{max}}{Y} f_{BTEX} C_{bio} \quad (5)$$

$$R_{O_2} = \frac{\partial C_{O_2}}{\partial t} = -\frac{C_{BTEX}}{K_{BTEX} + C_{BTEX}} \frac{C_{O_2}}{K_{O_2} + C_{O_2}} \frac{\mu_{max}}{Y} f_{O_2} C_{bio} \quad (6)$$

where,  $C_{BTEX}$ ,  $C_{O_2}$  and  $C_{bio}$  represent concentrations of BTEX, oxygen and biomass respectively,  $K_{BTEX}$  and  $K_{O_2}$  are the half-saturation constants of BTEX and oxygen,  $\mu_{max}$  is the maximum specific growth rate,  $Y$  denotes the specific yield of the reaction, and  $f_{BTEX}$  and  $f_{O_2}$  are the stoichiometric coefficients of Reactions 1-4.

Monod kinetics assumes a population of immobile BTEX oxidising aerobic microbes to be present in low concentrations. A double Monod kinetics with two multiplied Monod- terms for BTEX and oxygen is applied to mathematically model the growth of this microbial population. First-order kinetics is used to describe biomass decay. This simulates a microbial growth and degradation in the presence of BTEX and oxygen. A net growth rate may be obtained by subtracting decay from the growth. This

results in a permanent utilization of substrates even though biomass is constant (Cirpka and Valocchi, 2007, Mohamed et al, 2010):

$$\frac{\partial C_{bio}}{\partial t} = \frac{C_{BTEX}}{K_{BTEX} + C_{BTEX}} \frac{C_{O_2}}{K_{O_2} + C_{O_2}} \mu_{max} C_{bio} - k_{dec} C_{bio} \quad (7)$$

where,  $k_{dec}$  represents the first-order rate constant of biomass decay.

Monod kinetics expression assume that the transformation rate raises with the substrate concentration,  $C_{BTEX}$ , but as  $C_{BTEX}$  grows larger, the rate asymptotically attains a maximum value given by  $(\mu_{max}/Y)C_{bio}$ .

##### 3-2-2-Michaelis-Menten kinetics

Assuming that the biomass remains constant in time and space and further noting that sufficiently large amount of oxygen is present, Bekins et al. (1997) were assembled three constants in Equation 5 into one new constant named the maximum degradation rate expressed by  $v_M = \mu_{max} C_{bio}/Y$  (mg/L-day). This new simplified expression is a Michaelis-Menten kinetics relating to BTEX concentration. The Michaelis-Menten model is similar to the Monod equation without growth rate (Simpkins and Alexander, 1984; Bekins et al., 1997). This equation assumes a constant microbial population both in space and time.

$$\frac{\partial C_{BTEX}}{\partial t} = -v_M \frac{C_{BTEX}}{K_{BTEX} + C_{BTEX}} \quad (8)$$

##### 3-2-3-First-order kinetics

Bekins et al. (1997) and Schafer et al. (2005) presented a linear approximation for Equation 8. The selection of this expression to be applied for a particular case may depend on the relative values of  $C_{BTEX}$  and  $K_{BTEX}$ . In order to approximate Equation 8 using a first-order concept,  $C_{BTEX}$  has to be several times smaller than  $K_{BTEX}$  ( $C_{BTEX} \ll K_{BTEX}$ ):

$$\frac{\partial C_{BTEX}}{\partial t} = -\frac{v_M}{K_{BTEX}} C_{BTEX} \quad (9)$$

The constants in Equation 9 are often combined to give  $k_1 = v_M / K_{BTEX}$  ( $s^{-1}$ ); yielding the following expression for first-order kinetics model:

$$\frac{\partial C_{BTEX}}{\partial t} = -k_1 C_{BTEX} \quad (10)$$

where,  $k_1$  represents the first-order kinetics constant.

### 3-2-4-Zero-order kinetics

Zero-order kinetics is another simple expression for describing biodegradation process. This kinetics model is often used when  $C_{BTEX}$  in Equation 8 is several times greater than  $K_{BTEX}$  ( $C_{BTEX} \gg K_{BTEX}$ ):

$$\frac{\partial C_{BTEX}}{\partial t} = -v_M \quad (11)$$

### 3-3-Reactive transport equations

Equations 5 and 6 can be now substituted into the mass transport equations for BTEX and oxygen including a linear instantaneous adsorption process; yielding the following equations (Wheeler et al. 1987):

$$\phi R_{ret} \frac{\partial C_{BTEX}}{\partial t} - \frac{\partial}{\partial x} \left( D \frac{\partial C_{BTEX}}{\partial x} - u C_{BTEX} \right) = R_{BTEX} \quad (12)$$

$$\phi \frac{\partial C_{O_2}}{\partial t} - \frac{\partial}{\partial x} \left( D \frac{\partial C_{O_2}}{\partial x} - u C_{O_2} \right) = R_{O_2} \quad (13)$$

where,  $D$  denotes the dispersion tensor and  $u$  represents the incompressible velocity vector.

$R_{ret}$  in Equation 12 is called the retardation factor. It is expressed as follows:

$$R_{ret} = 1 + \frac{\rho_d K_d}{\phi} \quad (14)$$

where,  $\phi$  is referred to the porosity,  $\rho_d$  represents the bulk density of porous medium,  $K_d$  denotes distribution

coefficient defined by  $K_d = f_{oc} K_{oc}$ ,  $K_{oc}$  is the soil organic carbon to water partition coefficient of component,  $f_{oc}$  refers the mass fraction of natural soil organic carbon within the soil matrix.

### 4-Modelling tool

The partial differential equations describing reactive transport of biodegradable BTEX and oxygen consumption were solved using a general-purpose CFD package called PHOENICS (Spalding, 1981). The PHOENICS software is able to simulate all types of the kinetics models by providing extra coding in Q1 and GROUND files (Doulati Ardejani et al., 2004 a, b).

The mathematical equation which is solved by PHOENICS can be expressed as follows (CHAM, 2011):

$$\frac{\partial}{\partial t} (r_i \rho_i \phi_i) + \frac{\partial}{\partial x_j} \left( r_i \rho_i u_{j_i} \phi_i - r_i \Gamma_{\phi_i} \frac{\partial \phi_i}{\partial x_j} \right) = r_i S_{\phi_i} \quad (15)$$

where,  $\phi_i$  is any of the dependent variables of phase  $i$ ,  $t$  represents time,  $r_i$  refers volume fraction of phase  $i$ ,  $\rho_i$  stands for PHOENICS-term for density of phase  $i$ ,  $u_{j_i}$  denotes the velocity component in the  $x_j$  direction,  $\Gamma_{\phi_i}$  is diffusive exchange coefficient for  $\phi$  in phase  $i$ ,  $S_{\phi_i}$  represents source rate of  $\phi_i$ .

$S_{\phi_i}$  in Equation 15 incorporates all terms describing chemical and biological reactions except the physical transport mechanisms including diffusion and convection and transient term.

The extra terms in Equations 12 and 13 which are not included in PHOENICS governing equation, should be implemented in PHOENICS by introducing the appropriate setting for each term in the Q1 file in PIL (PHOENICS Input Language) coding and applying extra FORTRAN 99 coding in the GROUND subroutine (Doulati Ardejani et al., 2004 a, b).

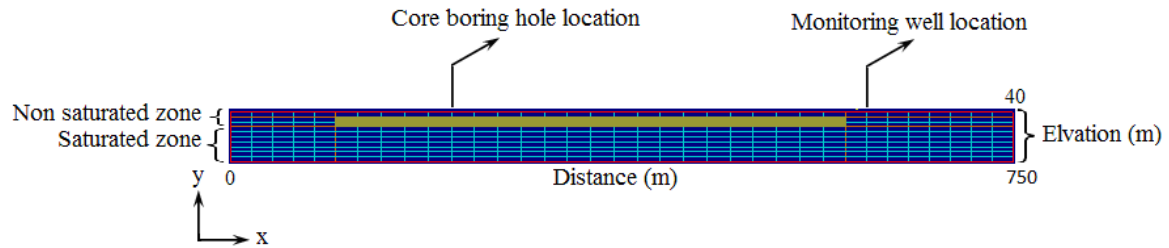


Figure 2. Two-dimensional finite volume grid (cross section A-B in Figure 1).

**4-1-Modelling Setting and performance**

A two-dimensional model was designed for the problem at hand. This model incorporates different kinetics expressions including Monod, Michaelis-Menten, first- and zero-order kinetics to BTEX governing transport equation to form a reactive transport scenario.

The two-dimensional cross-section of the simulated aquifer is 750 m horizontally (x direction) by 40 m vertically (y direction). The flow domain is discretised into 35×10 control volumes of size 18 m horizontally × 4 m vertically (Figure 2).

As Figure 2 shows, an immobile NAPL phase of 490 m × 8 m is maintained on the groundwater table, dissolving into the mobile pore water through a gradient law (modified from Schafer et al., 2005) given below:

$$\frac{\partial C_{mobile}}{\partial t} = k(C_{equilibrium} - C_{mobile}) \quad (16)$$

where,  $C_{equilibrium}$  denotes the maximum solubility and  $k$  represents a constant called dissolution rate.

The number of time steps used was 50. A total iteration of 1000 was assigned to the simulation. It was assumed that the flow system is saturated and the water flow is steady with an average velocity of  $1.13 \times 10^{-7}$  m/s. To perform a transient simulation, 50 time steps were considered.

The simulated aquifer had a permeability of 8.07 m/s. The dry density of aquifer materials was  $1.7 \text{ gr/cm}^3$ . A porosity of 0.4 was assumed for the flow medium. Longitudinal and transverse dispersivities were 15 m and 1 m respectively.

Retardation factors were 1.34, 2.06, 3.31 and 3.51 for benzene, toluene, ethylbenzene and xylene respectively. A fixed value of  $1.175 \times 10^{-6} \text{ s}^{-1}$  was considered as the rate coefficient of biomass decay.

No-flow boundary condition was assigned at the lower boundary of the model to simulate the impermeable layer of the aquifer. Fixed head boundary values equal to 34.5 m and 31.4 m were specified at the left and right sides of the model respectively.

An initial value of  $0 \text{ mg.l}^{-1}$  was maintained to describe the distribution of BTEX compound within the flow system at  $t = 0$ . In addition, initial values of  $5 \text{ mg.l}^{-1}$  and  $1.7 \text{ mg.l}^{-1}$  were considered for dissolved oxygen and biomass respectively. A first-type boundary condition was selected at the inlet of the model (zero for BTEX compound and biomass and  $5 \text{ mg.l}^{-1}$  for oxygen). A zero-concentration gradient boundary condition was assumed at the outlet of the model.

Other input parameters of the model are given in Table 1 and Table 2.

**Table 1. Model parameters used in the two-dimensional simulation (Goudar and Strevett, 1998; Park and Juan, 2000; Essaid et al., 2003; Schafer et al., 2005).**

Flow and transport parameters	
$K_{oc}$ of benzene	$7.94 \times 10^1 \text{ L/kg}$
$K_{oc}$ of toluene	$2.51 \times 10^2 \text{ L/kg}$
$K_{oc}$ of ethylbenzene	$5.37 \times 10^2 \text{ L/kg}$
$K_{oc}$ of xylene	$5.86 \times 10^2 \text{ L/kg}$
$f_{oc}$	0.001
Constant dissolution velocity of benzene	$4.86 \times 10^{-8} \text{ s}^{-1}$

Constant dissolution velocity of toluene	$1.16 \times 10^{-8} \text{ s}^{-1}$
Constant dissolution velocity of ethylbenzene	$6.36 \times 10^{-8} \text{ s}^{-1}$
Constant dissolution velocity of xylene	$5.67 \times 10^{-8} \text{ s}^{-1}$
Maximum solubility of benzene	$1780 \text{ mg.l}^{-1}$
Maximum solubility of toluene	$520 \text{ mg.l}^{-1}$
Maximum solubility of ethylbenzene	$152 \text{ mg.l}^{-1}$
Maximum solubility of xylene	$198 \text{ mg.l}^{-1}$
Benzene half-saturation constant	$2.690 \text{ mg.l}^{-1}$
Toluene half-saturation constant	$3.253 \text{ mg.l}^{-1}$
Ethylbenzene half-saturation constant	$1.288 \text{ mg.l}^{-1}$
Xylene half-saturation constant	$4.681 \text{ mg.l}^{-1}$
Maximum specific growth rate for benzene	$5.69 \text{ e}^{-5} \text{ s}^{-1}$
Maximum specific growth rate for toluene	$1.02 \text{ e}^{-4} \text{ s}^{-1}$
Maximum specific growth rate for ethylbenzene	$5.86 \text{ e}^{-5} \text{ s}^{-1}$
Maximum specific growth rate for xylene	$6.69 \text{ e}^{-5} \text{ s}^{-1}$
Specific yield of the reaction for benzene	$0.477 \text{ mg.mg}^{-1}$
Specific yield of the reaction for toluene	$0.427 \text{ mg.mg}^{-1}$
Specific yield of the reaction for ethylbenzene	$0.272 \text{ mg.mg}^{-1}$
Specific yield of the reaction for xylene	$0.331 \text{ mg.mg}^{-1}$

**Table 2. Weathered gasoline weight fraction (Park and Juan, 2000).**

	Toluene	Ethylbenze	Xylenes
0.01	0.10	0.03	0.13

#### 4-2-Model verification

The results of numerical finite volume model using PHOENICS commercial package was first verified by those results obtained from a two dimensional finite element modelling of reactive transport problem which was developed by Pickens and Lennox (1976). The model was further verified by the field data measured at an unconfined aquifer in the Pump station

area of Tehran oil refinery, Iran to predict the fate and reactive transport of biodegradable BTEX plume. Although not given here, a close agreement was achieved between model predictions and field measurements with an average error of 5%. The verified model was then used to perform a sensitivity analysis.

#### 4-3-Sensitivity analysis

Many uncertainties are associated with groundwater contamination description due to the variability of the aquifer characteristics and contaminant spatial distribution. In natural attenuation assessments, the impact of these uncertainties on plume geometry and concentration distribution is important, particularly relating to potential risks associated with the contamination (Gribb et al., 2002, Suarez and Rifai, 2004). Various methods are used to assess this uncertainty. One of these methods is sensitivity analysis. This method determines the effect of model input parameters on model output quantity. A sensitivity analysis is required to improve insight into which model parameters govern modelling predicted quantities.

To consider the response of the model to changes in the parameter values used for modelling, the sensitivity of the model to changes in the dispersivity, distribution coefficient, parameters of Monod, Michaelis-Menten, first- and zero-order kinetics on the contaminant plume were examined by performing several simulations.

The first simulation was performed to consider the sensitivity of the model to changes in dispersivity values. The dispersivities ranged from 0.5 m to 15 m.

The concentration distributions obtained with different dispersivity values, for a time period of 50 years and a distribution coefficient of 0 are shown in Figures 4 to 8. The results show that as the value of dispersivity increases, the contaminants shift further through the groundwater flow medium. This means that the dispersion

process is an important mechanism affecting on solute fate and transport. In addition, an increase in dispersivity decreased the concentration gradient. Since the groundwater flow was assumed to be

horizontal, an increase in the transverse dispersivity causes the contaminants to shift much further toward the lower boundary of the model (Pickens and Lennox, 1976).

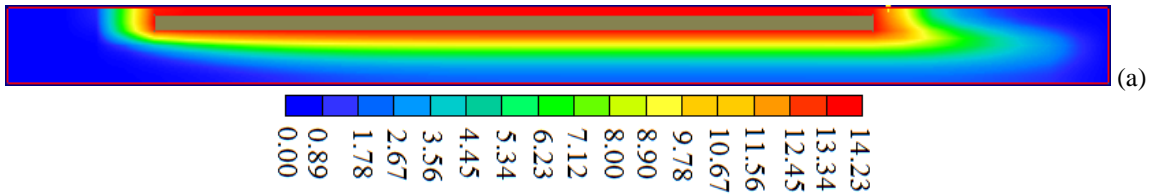


Figure 4. Concentration distribution of benzene with a dispersivity value of  $\alpha_L = \alpha_T = 0.5m$  and for a time period of 50 years.

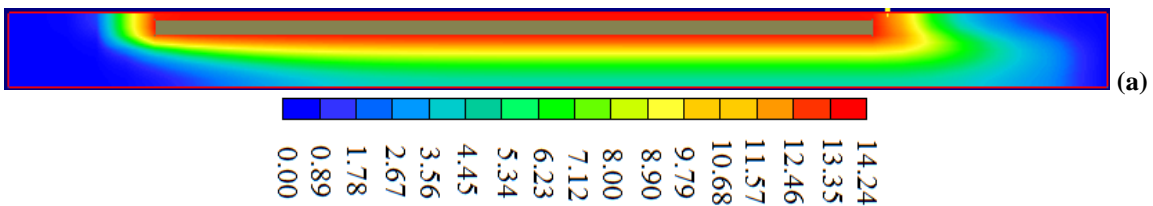


Figure 5. Concentration distribution of benzene with a dispersivity value of  $\alpha_L = \alpha_T = 1m$  and for a time period of 50 years.

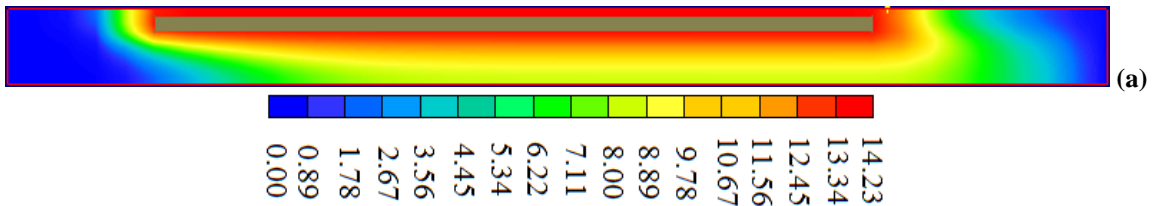


Figure 6. Concentration distribution of benzene with a dispersivity value of  $\alpha_L = \alpha_T = 2m$  and for a time period of 50 years.

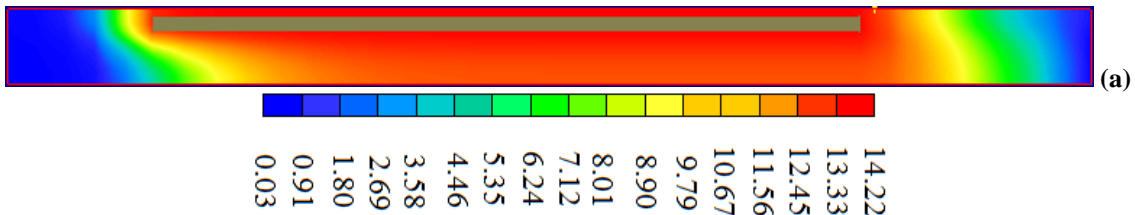


Figure 7. Concentration distribution of benzene with a dispersivity value of  $\alpha_L = \alpha_T = 5m$  and for a time period of 50 years.

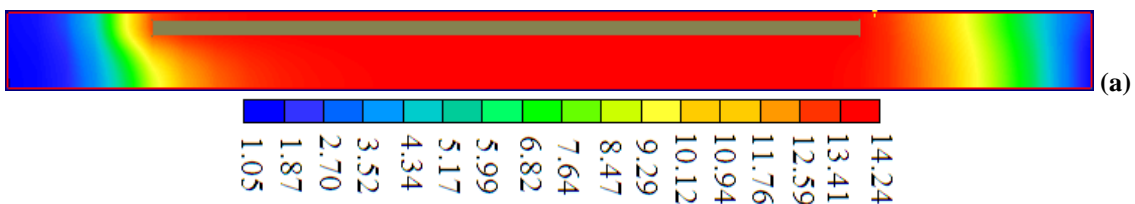


Figure 8. Concentration distribution of benzene with a dispersivity value of  $\alpha_L = \alpha_T = 15m$  and for a time period of 50 years.



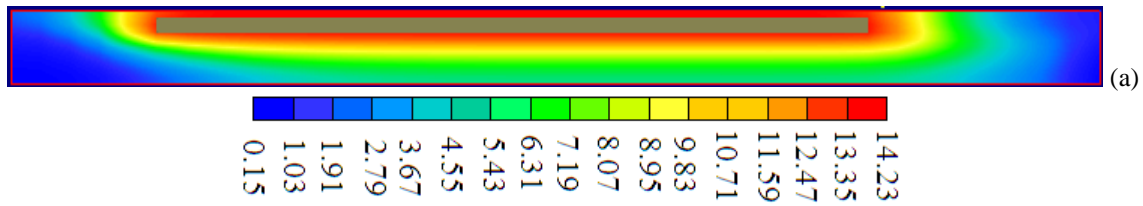


Figure 9. Concentration plume of benzene with a distribution coefficient of 1.34.

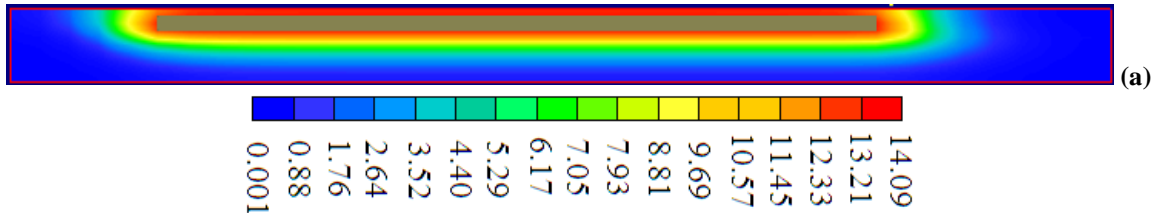


Figure 10. Concentration plume of benzene with a distribution coefficient of 4.37.

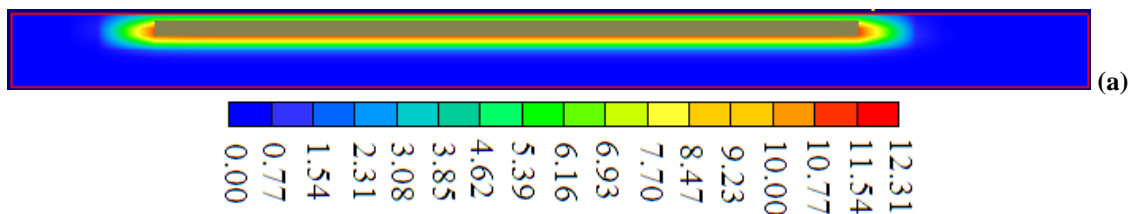


Figure 11. Concentration plume of benzene with a distribution coefficient of 34.6.

Second simulation takes into consideration the effect of linear adsorption on solute transport problem. Figures 9 through 11 show the effect of varying the value of distribution coefficient on the concentration distribution for dispersivity values of  $\alpha_L = 15m$  and  $\alpha_T = 1m$ , and for a time period of 50 years. Contaminant movement is very slow for large values of  $K_d$  in the flow direction.

The third simulation was performed to consider the sensitivity of the model to changes in parameters of Monod kinetics. To carry out the simulation, two parameter sets are selected. The first set of parameters generally overestimates biodegradation by a factor 2 in the maximum specific growth rate and the specific yield of the reaction and a factor 0.5 in half-saturation constant of BTEX and oxygen. The second set underestimates biodegradation by a factor 0.5 in the maximum specific growth rate and the specific yield of the reaction and a factor 2

in half-saturation constant of BTEX and oxygen.

Results of sensitivity analysis on parameters of Monod kinetics show this approach is not very sensitive to these parametric changes because no significant changes were detected on BTEX plume behaviour (Figures 12 and 13).

This can be explained that aerobic biodegradation is not limited by microbial kinetics, but by the dispersive mixing of contaminated water with clean water containing oxygen in aquifer. This phenomenon is the process of mechanical dispersion that causes mixing of dissolved contaminants and electron acceptors. In Monod kinetics, the biodegradation takes place only when BTEX and oxygen are available at the same time and place. According to Schafer et al. (2005), the plumes simulated by poorly parameterised Monod kinetics are better consistent with the actual plume than the plumes determined with the simplified methods.



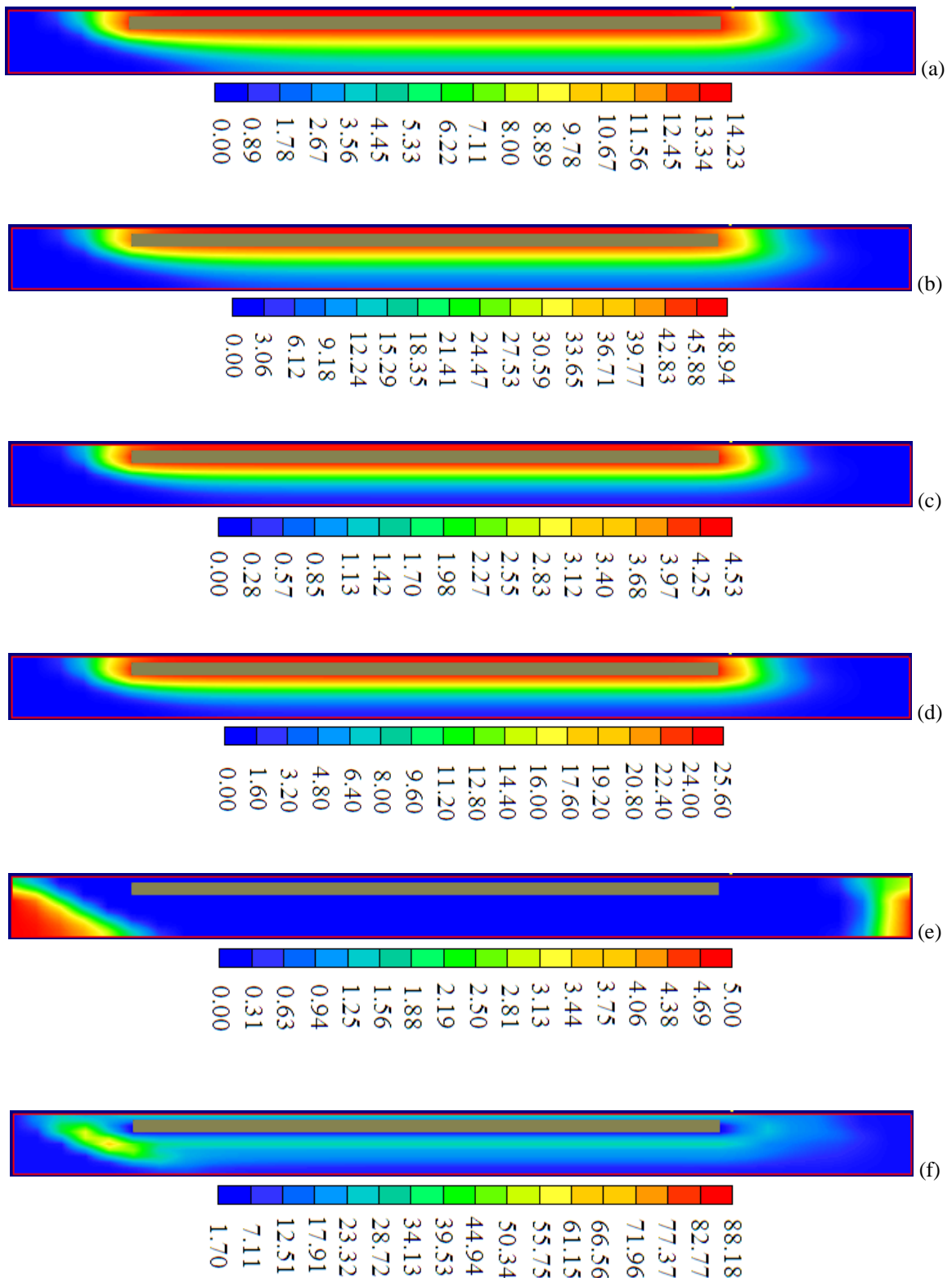
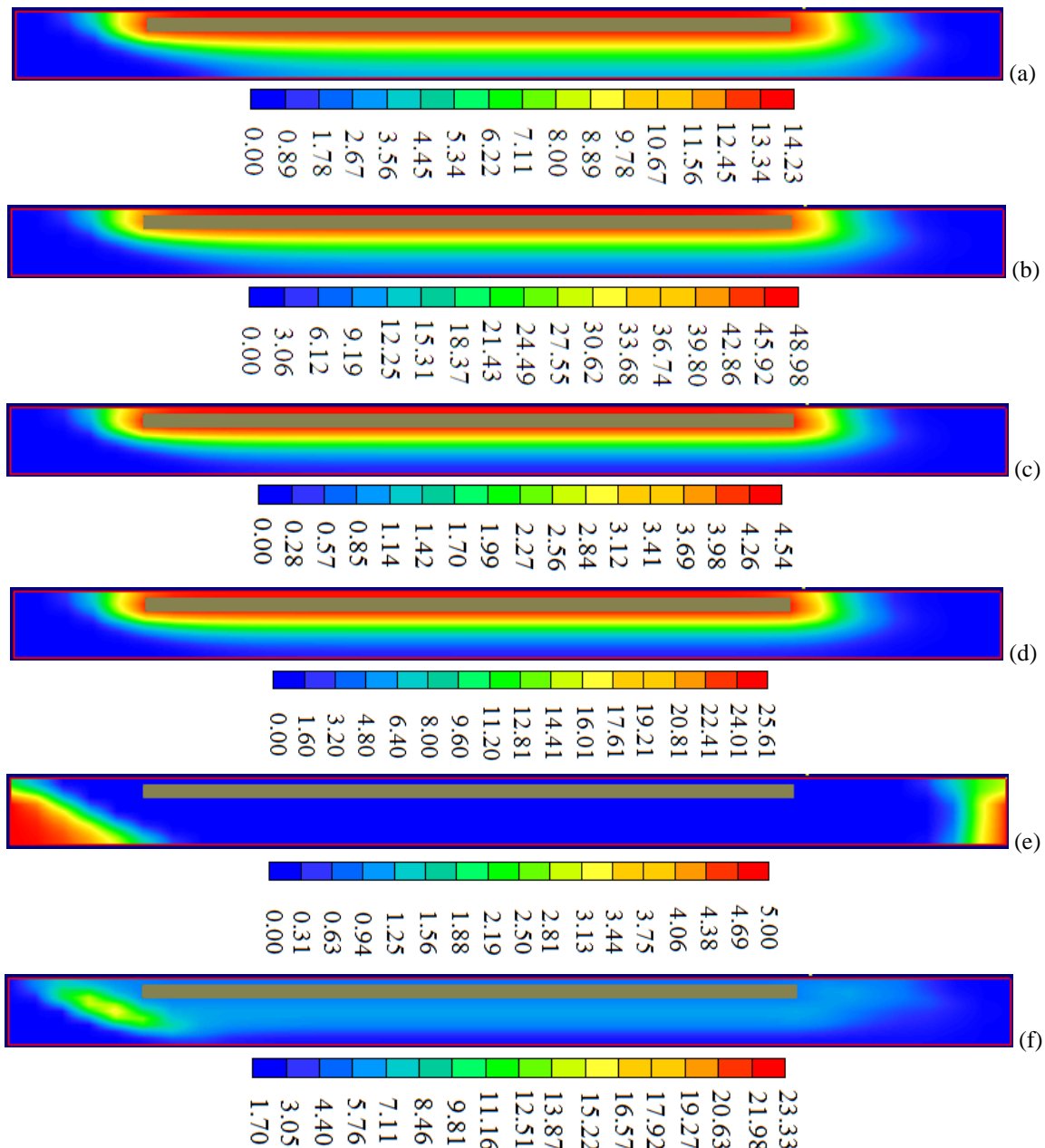


Figure 12. Two-dimensional simulation cross-section: (a), (b), (c) and (d) are concentration distribution of benzene, toluene, ethylbenzene and xylene after 50 years of the simulation using the overestimated Monod approach. (e) and (f) are concentration distribution of oxygen and biomass after 50 years respectively.



**Figure 13. Two-dimensional simulation cross-section: (a), (b), (c) and (d) are concentration distribution of benzene, toluene, ethylbenzene and xylene after 50 years of the simulation using the underestimated Monod approach. (e) and (f) are concentration distribution of oxygen and biomass after 50 years respectively.**

The fourth simulation was run to check the sensitivity of the model to changes in parameters of Michaelis-Menten kinetics. To perform this scenario, two parameter sets are chosen. The first set of parameters generally overestimates biodegradation by a factor 2 in the lumped maximum degradation rate and a factor 0.5 in half-saturation constant of BTEX and oxygen. The second set underestimates biodegradation by a factor 0.5 in the

lumped maximum degradation rate and a factor 2 in half-saturation constant of BTEX and oxygen.

Unlike Monod kinetics, this approach is sensitive to changes in its parameters. The first set of parameters causes a reduction in concentration and length of plumes, while using the second set, plumes can be simulated with more concentration and expansion (Figures 14 and 15).

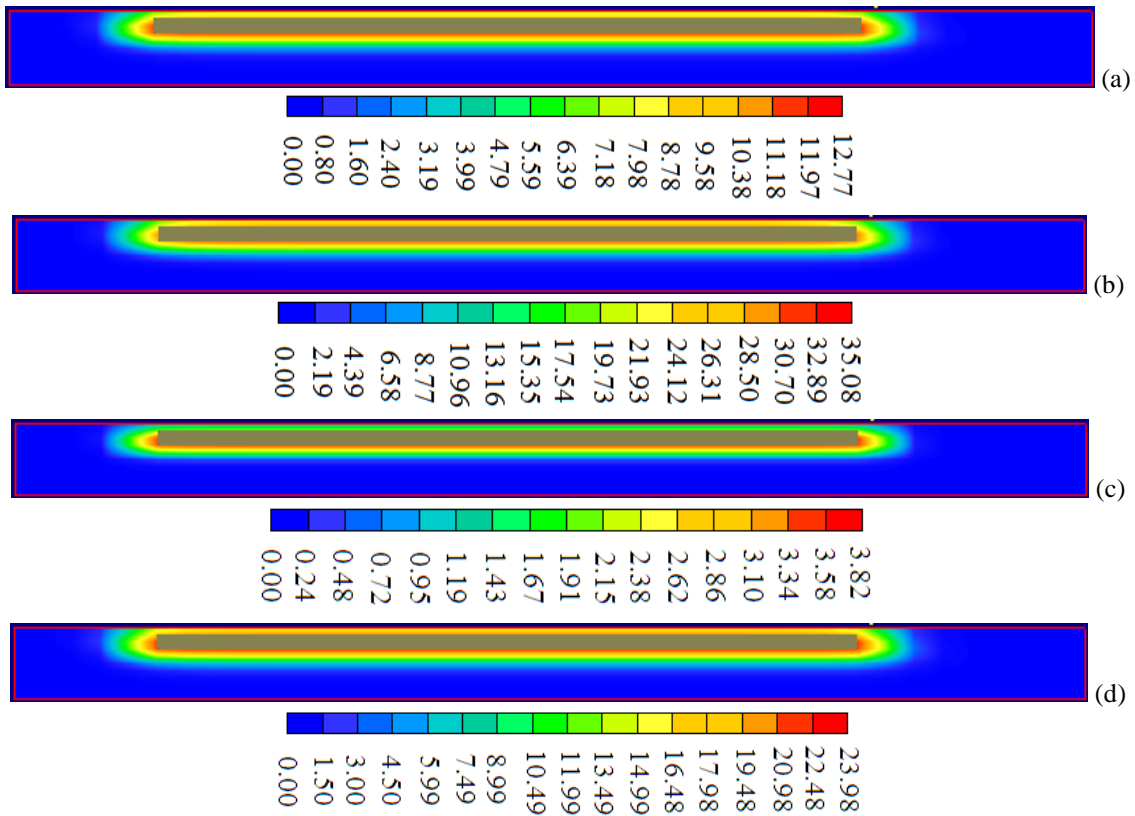


Figure 14. Two-dimensional simulation cross-section: (a), (b), (c) and (d) are concentration distribution of benzene, toluene, ethylbenzene and xylene after 50 years of the simulation using the overestimated Michaelis-Menten kinetics.

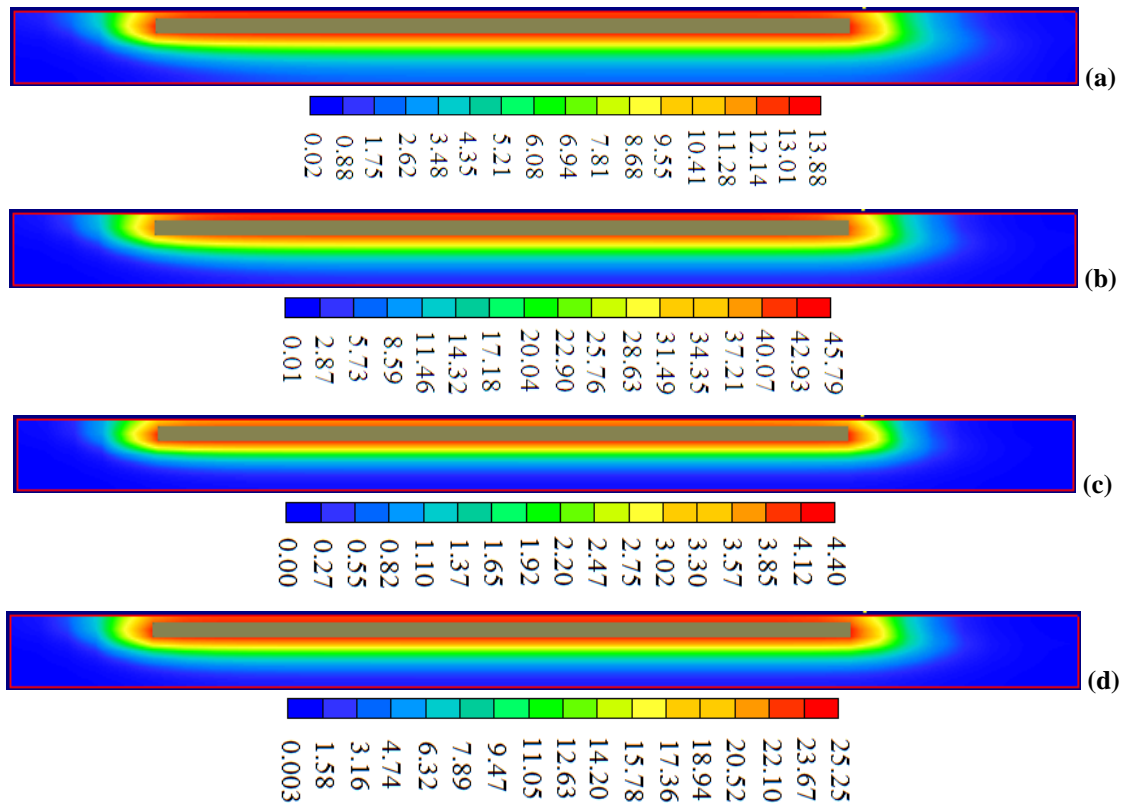


Figure 15. Two-dimensional simulation cross-section: (a), (b), (c) and (d) are concentration distribution of benzene, toluene, ethylbenzene and xylene after 50 years of the simulation using the underestimated Michaelis-Menten kinetics.

Fifth scenario includes sensitivity of the model to changes in first-order rate constant of first-order kinetics model. Similar to the Michaelis-Menten approach, the model is also sensitive to changes in this rate constant. Concentration and

expansion of plumes decrease with doubling of the first-order rate constant. However, these plumes expand further by decreasing the first-order rate constant to half. (Figures 16 and 17).

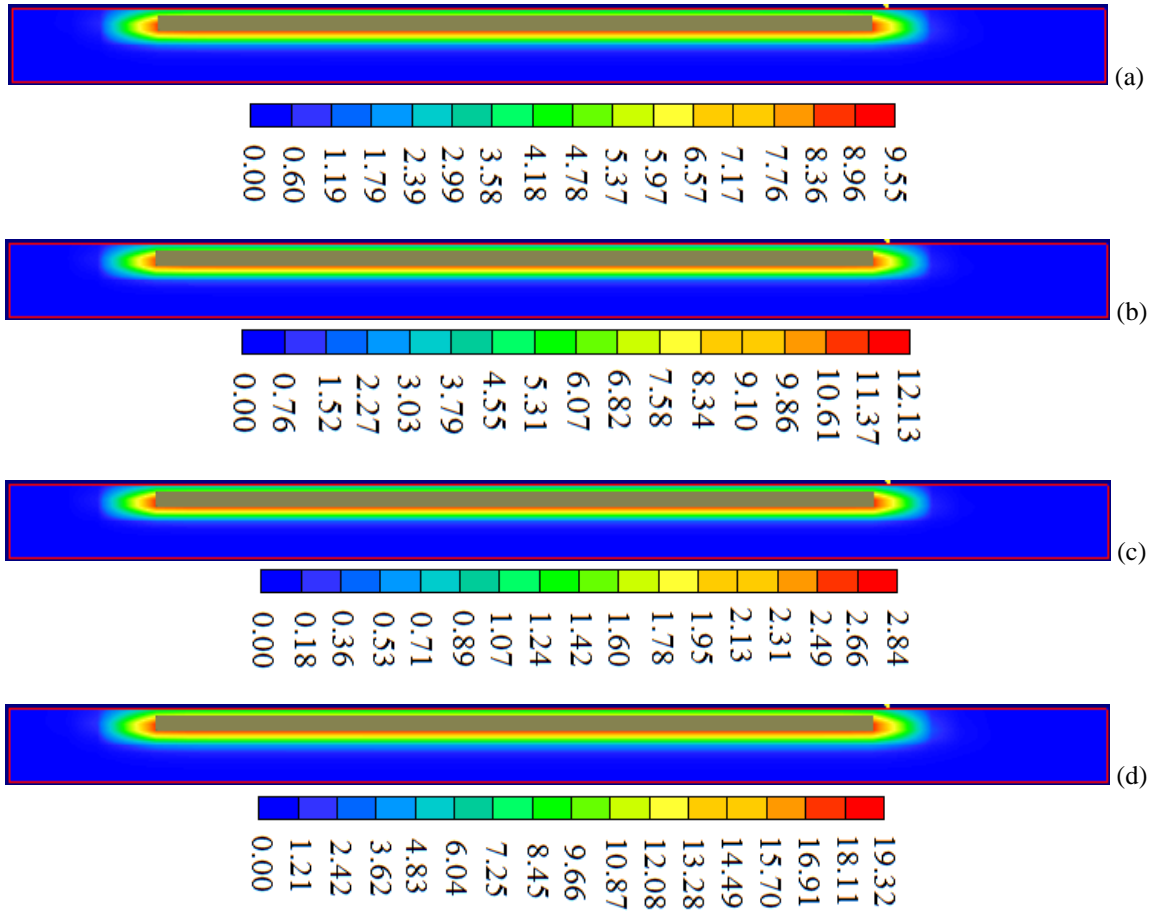


Figure 16. Two-dimensional simulation cross-section: (a), (b), (c) and (d) are concentration distribution of benzene, toluene, ethylbenzene and xylene after 50 years of the simulation using the overestimated first order kinetics.

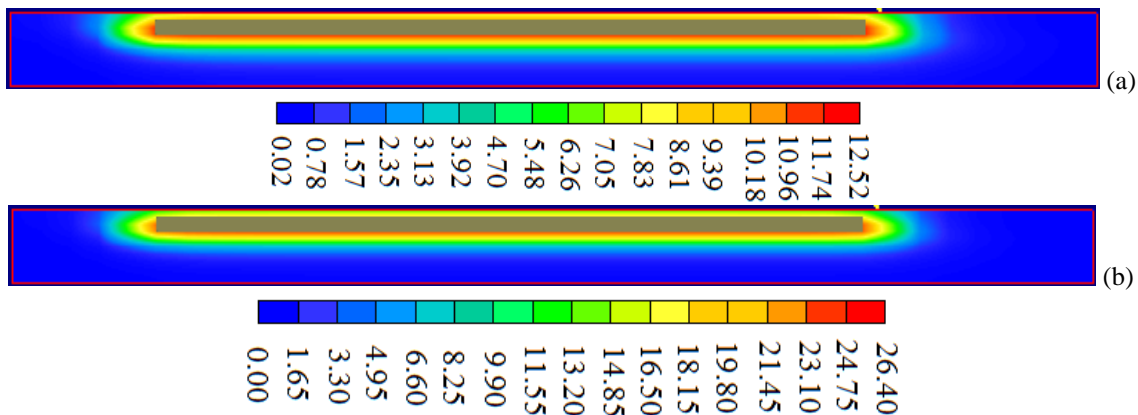


Figure 17. Two-dimensional simulation cross-section: (a), (b), (c) and (d) are concentration distribution of benzene, toluene, ethylbenzene and xylene after 50 years of the simulation using the underestimated first-order kinetics.

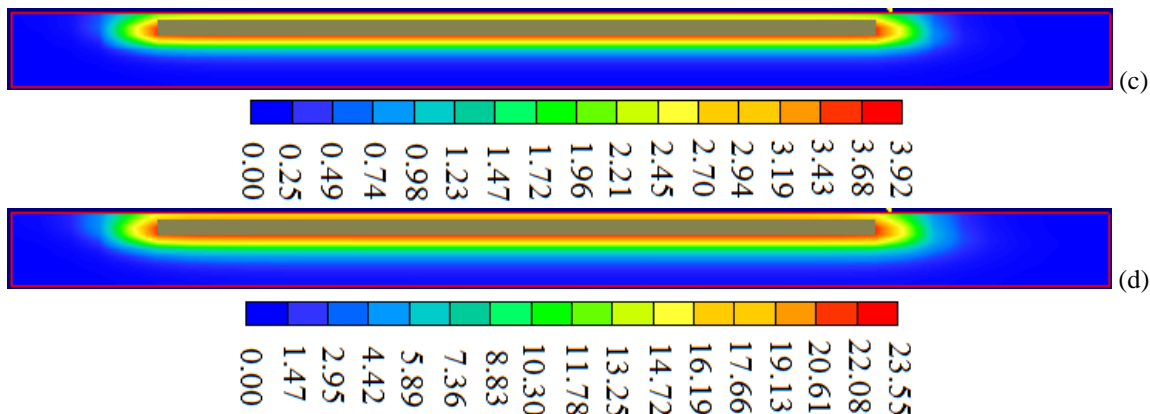


Figure 17. Two-dimensional simulation cross-section: (a), (b), (c) and (d) are concentration distribution of benzene, toluene, ethylbenzene and xylene after 50 years of the simulation using the underestimated first-order kinetics.

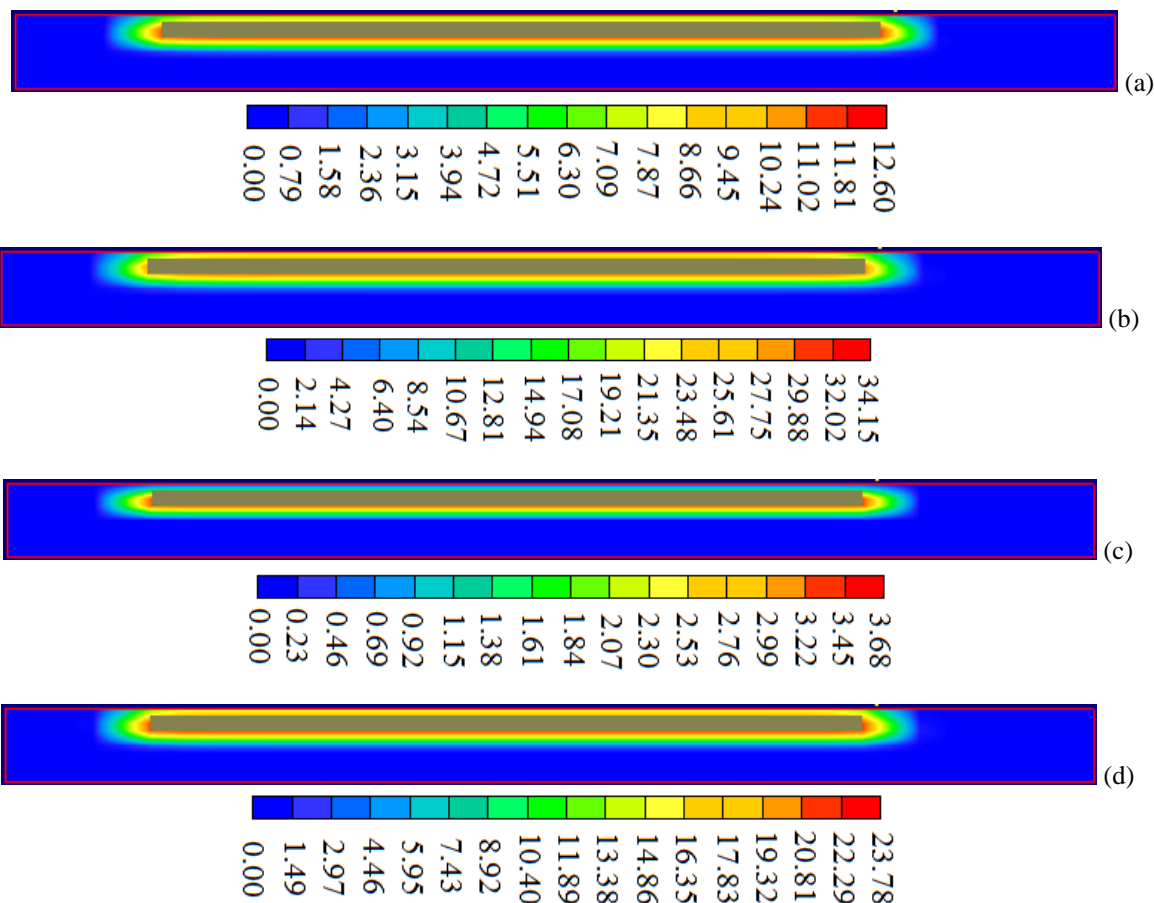
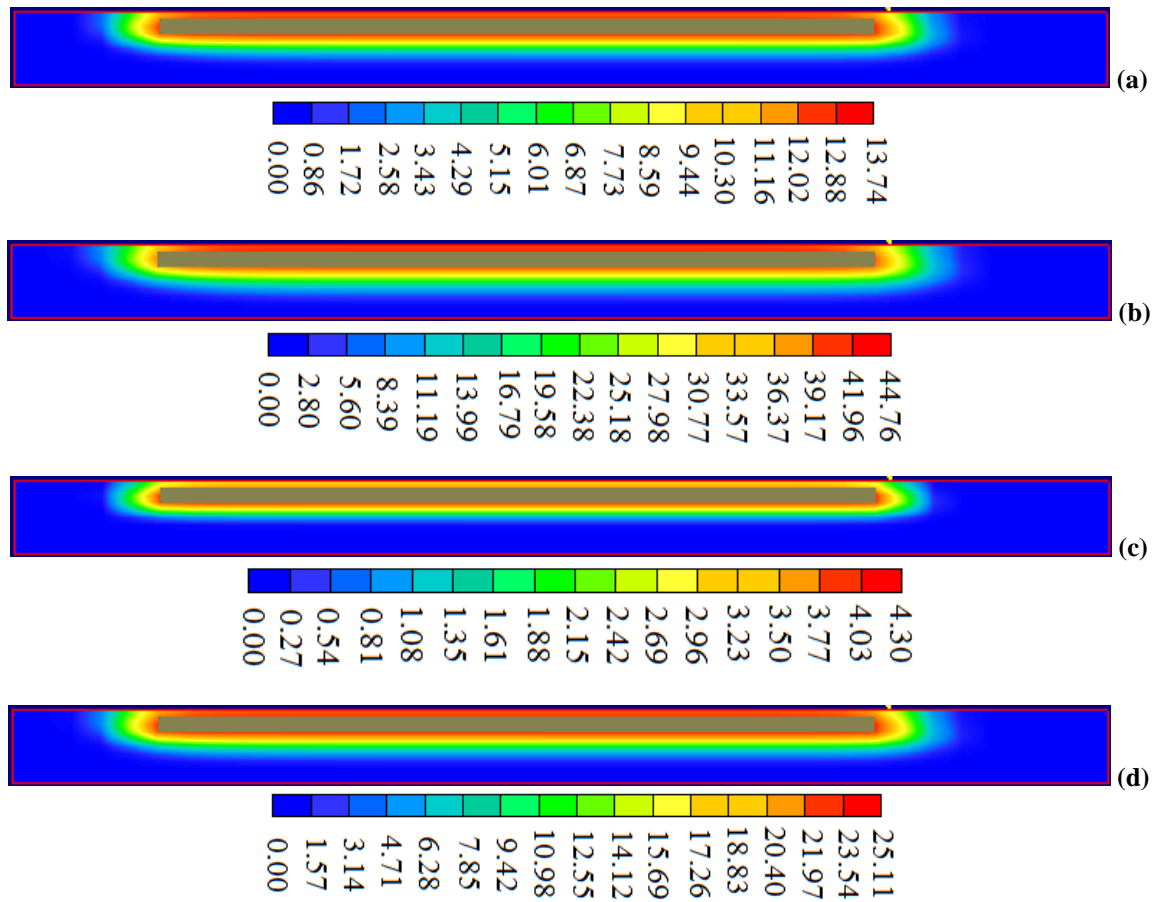


Figure 18. Two-dimensional simulation cross-section: (a), (b), (c) and (d) are concentration distribution of benzene, toluene, ethylbenzene and xylene after 50 years of the simulation using the overestimated zero order kinetics.

The last simulation was run to investigate the sensitivity of the model to changes in zero-order rate constant. This approach, like Michaelis-Menten and first-order kinetics approaches, is sensitive to changes in zero-order kinetics constant.

Concentration and length of the predicted plumes decrease by doubling of the zero-order rate constant. In contrary, reduction in this parameter to half causes an increase in concentration and length of plumes (Figures 18 and 19).



**Figure 19. Two-dimensional simulation cross-section: (a), (b), (c) and (d) are concentration distribution of benzene, toluene, ethylbenzene and xylene after 50 years of the simulation using the underestimated zero order kinetics.**

## 5-Conclusions

The results obtained from a numerical model for simulation of fate and transport of BTEX in an unconfined aquifer system in the Pump station area of Tehran Oil Refinery has been presented. Particular consideration has been given to the sensitivity of the modelling outputs to changes in the model major parameters. In this paper the effects of changing the values of parameters such as the dispersivity, distribution coefficient, parameters of Monod, Michaelis-Menten, first-order and zero-order kinetics models on the contaminant plume have been examined. The following main conclusions are obtained from this work:

- The increase in the dispersivity shifted further the contaminants through the groundwater flow medium. In addition, an increase in the dispersivity

decreased the concentration gradient. Since the groundwater flow was assumed to be horizontal, an increase in the transverse dispersivity causes the contaminants to shift much further toward the lower boundary of the model. This means that the dispersion process is an important mechanism affecting on solute fate and transport.

- Contaminant movement is very slow for large values of distribution coefficient in the flow direction.
- Results of sensitivity analysis on parameters of Monod kinetics show that the model is not very sensitive to changes in these parameters because no significant changes were detected on BTEX plume behavior. This may due to the fact that aerobic biodegradation is not limited by microbial kinetics, but by the dispersive mixing of

contaminated water with the clean water containing oxygen in aquifer. This phenomenon is the process of mechanical dispersion that causes mixing of dissolved contaminants and electron acceptors. Monod kinetics assumes that biodegradation takes place only when BTEX and oxygen are available at the same time and place. Thus, the plumes simulated by the Monod kinetics are better consistent with the actual plume than the plumes calculated with the simplified approaches.

- Unlike Monod kinetics, Michaelis-Menten kinetics is sensitive to changes in its parameters. The first set of parameters simulates a reduction in concentration and length of plumes,

while second set causes further concentration and more expansion.

- Concentration and length of contaminant plumes was decreased by increasing first- and zero-order rate constants.

The results of this sensitivity analysis provide a rational way for determining which model parameters are more critical when it is desired to control the pollutant transportation mechanisms.

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