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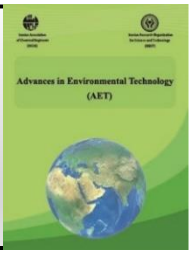

Risk assessment of hydrocarbon contaminant transport in vadose zone as it travels to groundwater table: A case study

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ABSTRACT

In this paper, a modeling tool for risk assessment analysis of the movement of hydrocarbon contaminants in the vadose zone and mass flux of contamination release into the groundwater table was developed. Also, advection-diffusion-reaction equations in combination with a three-phase equilibrium state between trapped air, soil humidity, and solid particles of unsaturated soil matrix were numerically solved to obtain a one dimensional concentration change in respect to depth of soil and total mass loading rate of hydrocarbons into the groundwater table. The developed model calibrations by means of sensitivity analysis and model validation via data from a site contaminated with BTEX were performed. Subsequently, the introduced model was applied on the collected hydrocarbon concentration data from a contaminated region of a gas refinery plant in Booshehr, Iran. Four different scenarios representing the role of different risk management policies and natural bio-degradation effects were defined to predict the future contaminant profile as well as the risk of the mass flux of contaminant components seeping into the groundwater table. The comparison between different scenarios showed that bio-degradation plays an important role in the contaminant attenuation rate; where in the scenarios including bio-degradation, the contaminant flux into the ground water table lasted for 50 years with the maximum release rate of around 20 gr per year while in the scenarios without including bio-degradation, 300 years of contaminant release into groundwater table with the maximum rate of 100 gr per year is obtained. Risk assessment analysis strongly suggests a need for bioremediation enhancement in the contaminated zones to reduce the contaminant influx to groundwater.

1. Introduction

Groundwater is located beneath the ground surface in soil pore spaces and in the fractures of rock formations. Pollutants released into the soil work their way down into the groundwater, polluting it and triggering certain problems. These underground contaminants, one of the most common of these problems, have beset the use of groundwater worldwide. Therefore, any risk assessment tools could play an essential role in identifying which sites are more likely to infect the groundwater [1]. Hydrocarbon contaminants that permeate to the lower levels, transit from the vadose zone to reach the groundwater table. In their pathway, it is important to consider soil types and pollutant properties in the model, which contain an immense range of properties [2, 3]. Volatile organic compounds (VOCs) are mostly non-aqeous phase liquids (NAPLs) and have leaked randomly into the vadose zone from different sources, i.e., in this study from the underground facilities of a gas refinery plant. NAPL contaminants from various sources which percolate in the vadose zone can remain there for decades and act as a long term contaminated source [4, 5] presented one of the first analytical models for contaminant transport in the vadose zone and it was later developed by [6]. In addition,

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many extensions of their assumptions as well as some new assumptions have been provided by other researchers [7]; [8, 4] evaluated analytical and numerical mathematical models for the transport of VOCs in the unsaturated zone, especially those that have been recently developed, and provided a comparison of the results. They concluded that these models were mostly used for NAPL sources rather than VOCs. They also mentioned the lack of laboratory and field data for validation. Published one or three dimensions numerical models and commercial codes have also been evaluated by [9] and the results indicated that the most of these studies investigated pollution transport in the unsaturated zone in the aqueous phase only. The three dimensional models need more input data; nevertheless, [3] concluded that in some common states a one dimensional (1D) model gives an acceptable result, especially when the contaminated area is shallow or large and has high water contents or a high biodegradation constant. However, the input parameters of a one dimensional model are less than that of a three dimensional model. Even though the assumptions used in a 1D model overestimate the risk, this aspect is not considered as a negative point. [9] also mentioned that in the majority of these models, the contaminant transport modeling was independent of each of the other compounds when there was a mixture of compounds as contaminants. Contaminants located in the voids within the soil, in addition to being dissolved in the pore water, are adsorbed into the soil particles [5, 7] or replaces the air trapped in the soil [10] and the degradation process can occur in all phases [11, 12]. A 1D contaminant transport model in the vadose zone that takes into account the effect of immobile water content has been investigated by [13]. They solved a dual porosity model whereby moisture is split into two parts, θ_m and θ_{im}, indicating mobile and immobile soil moisture, respectively. Finally, they were unable to achieve a clear result regarding whether immobile humidity should be considered or ignored. Their findings only noted that the immobile moisture affects the contaminant transport. A study of one dimensional hydraulic transport of contaminants in the vadose zone in both cases of steady state and transient flow were examined by [14]. They introduced the dimensionless Damköhler number for sorption and degradation kinetics for characterization and comparison of soil contamination profile. They concluded that a steady state flow conditions along with assuming a constant Darcy velocity in the soil does not cause significant problems, with the exception of special cases such as extreme infiltration rate. In this study, a one dimensional model of the hydrocarbon contaminant's movement in the vadose zone is described. This model was used in four different scenarios representing different risk management policies over the measured soil hydrocarbon content of a gas refinery plant. To obtain the field data of the hydrocarbon contaminant concentration in the unsaturated zone, a soil sampling and laboratory analysis of the samples were conducted.

2. Materials and Methods

The field sampling and analyzing was done in a gas refinery plant located in the SPGC area, Booshehr, Iran. Different locations of the plant were determined to be contaminated by the release of hydrocarbon contaminants from underground pipes. To begin with, a map of the suspected locations was prepared. The contaminated areas were dug and those with a higher contamination level were drilled with an excavation machine. During the drilling, soil samples were taken from various depths (roughly at one meter intervals) and were kept in a sealed container and placed in a cold box; they were then transferred to the refrigerator to be kept until the lab tests could be performed. The soil samples were refluxed with methylene chloride for 30 minutes. The extracted solution was then injected to the gas chromatography–mass spectrometry (GC-MS) to determine the components spectrum of the contaminated soil (Agilent Technologies 6890N GC- Agilent Mass selective detector 5973N). A HP-5MS column, 30 m in length and 0.25 mm in diameter, was used. The instrument condition was: a 250 °C injection temperature, 100 °C for 2 min; then the temperature was increased by 10 °C/min for 20 min. Helium was used as a carrier gas in 1 ml/min and run in a split-less mode. A mass detector was run at 230 °C in an ion source and at 150 °C for the mass analyzer. The total petroleum hydrocarbon (TPH) analysis was also performed on the collected sample soil according to US EPA Methods 413.2 and 418.1 and ASTM Method D3921. The TPH was determined by an IR at 2940 cm^{-1} (InfraCal TOG/TPH Analyzer -Wilkins Enterprise). Most of the compounds found in the contaminated soil were hydrocarbons that have a boiling temperature between 50-250 °C. According to the European Union definition, they are considered VOCs [4].

3. Model Description

In this section, a one dimensional vertical transport contaminant is described in three phases. The contaminant movement within and between the liquid, gas, and solid phase is considered as: (1) a solute dissolved in water, (2) a gas in the vapor phase, and (3) as an adsorbed compound in the solid phase. A conceptual sketch of the most effective mechanisms that are considered in the simulation is shown in Fig. 1. The model is based on the following assumption sets:

(i) Soil is homogenous with constant properties,
(ii) Steady-state flow pattern is considered; by means of Darcy velocity is constant with time ($\frac{dq}{dt} = 0$),
(iii) Linear, reversible, and isotherm equilibrium partitioning is held between phases,

(iv) Non-aqueous phase liquid transport is not considered,

(v) Advection and degradation are considered in the liquid phase, diffusion in the gas phase and adsorption in the solid phase, and,

(vi) It is assumed that the non-aqueous phase is available in the immobile parts of the soil. This means that only the aqueous phase is transported and NAPL is not moved by gravity or other driving forces such as leakage of a new amount of pollutant infiltration. This assumption is more reasonable in the low NAPL concentration.

3.1. Governing Equations

Based on the available data and the aim of our study, a one dimensional model was used to predict a contaminant concentrations profile and groundwater infiltration. In this model, only the vertical transport of dissolved contaminants is modeled in three phases of gas, liquid, and solid which are indicated with C_g, C_l and C_s, respectively. The concentration in the liquid phase is obtained by solving the following equation that accounts for advection and considering first-order degradation:

$$\frac{\partial C_l}{\partial t} = -\nu \frac{\partial C_l}{\partial z} - \lambda C_l \quad (1)$$

where, C_l (M L^{-3}) shows the solute concentration in the water phase, λ (T^{-1}) is the first-order degradation rate, and ν (L T^{-1}) is the seepage velocity that is given by:

$$\nu = \frac{q}{\theta_w} \quad (2)$$

where, q (L T^{-1}) stands for the water infiltration rate and θ_w (-) is the volumetric water content [15, 8, 3].
The gas phase concentration of contaminant is determined by the following diffusion equation:

$$\frac{\partial C_g}{\partial t} = D_P \frac{\partial^2 C_g}{\partial z^2} \quad (3)$$

where, C_g (M L^{-3}) is the contaminant concentration in the gas phase and D_p is the gaseous diffusion coefficient in the air-filled pore spaces as given by:

$$D_P = D_{air} \frac{{\theta_a}^{7/3}}{\emptyset^2} \quad (4)$$

where, D_{air} (L^2 T^{-1}) is the diffusion coefficient in the air, θ_a (-) is the volumetric air content, and $\emptyset$ (-) is the porosity. Eq. (4) is an expression of the Millington Equation [16] for the gaseous diffusion coefficient in the air-filled pore spaces [17, 15, 8].
The total mass of contaminant in the soil mass M_T (M M^{-1}) then can be expressed as:

$$M_T = [\theta_w C_l + \theta_a C_g + \rho_b C_s] \quad (5)$$

where, C_s (M M^{-1}) is the contaminant concentration in the solid phase [15]. Equilibrium partitioning between the concentrations of different phases can be obtained as:

$$C_1 = \frac{M_T}{R'} \quad (6)$$

$$C_g = K_H C_l \quad (7)$$

$$C_s = \frac{K_d M_T}{R'} \quad (8)$$

Where:

$$R' = R\theta_w + K_H \theta_a \quad (9)$$

$$R = 1 + \frac{\rho_b}{\theta_w} K_d \quad (10)$$

$$K_d = K_{oc} f_{oc} \quad (11)$$

In the above equations, R (-) is the retardation coefficient, K_d (L^3 M^{-1}) is the distribution coefficient, K_H (-) is the dimensionless Henry's constant, ρ_b (M L^{-3}) is the bulk density, K_{oc} (L^3 M^{-1}) is the partition coefficient between the contaminant and natural organic matter, and f_{oc} (-) is the fraction organic carbon content of the soil [15, 3].

3.2. Solution Procedure

The partial differential equations (1) and (3) are solved by the Crank-Nicholson method in the finite difference approach. A zero concentration gradient for gas concentration was assumed for the lower boundary condition at the groundwater table. Also, contaminant concentration in the atmosphere above the soil surface was assumed to be zero. According to Eq. (6), if C_l in each time and location is higher than the maximum capacity of water solubility ($C_{l\_soluble}$) then C_l was made equal to $C_{l\_soluble}$ to calculate C_g. Mass loading of contamination $\dot{m}_{loading}$ (M T^{-1}) to groundwater was determined according to the following equation:

$$\dot{m}_{loading} = C_l|_{@\ groundwater\ table} . A . q \quad (12)$$

Where $C_l|_{@\ groundwater\ table}$ is the water phase concentration at the groundwater table, A (L^2) is the contaminated zone area, and q (L T^{-1}) is the infiltration rate. Where $C_l|_{@\ groundwater\ table}$ is the water phase concentration at the groundwater table, A (L^2) is the contaminated zone area, and q (L T^{-1}) is the infiltration rate.

4. Model Application

4.1 Model Validation

The model was validated using the BTEX released data by [3]. In their case study, free phase fuel oil had been leaked from a fuel oil tank for an unknown period. The pipe was 0.5 m below the ground surface and the contaminant source was estimated to have an area of 5×5 m^2, with residual phase contamination extending to a depth of 3 m below ground surface. The source zone was considered immobile. The contaminant source contained approximately 320 kg fuel oil. The soil samples of the source zone contained approximately 0.1% BTEX (Benzene, Toluene, Ethylbenzene, and Xylenes). The mass fraction of BTEX in the pore gas samples was reported to be around 1–3%; the average source zone concentration in the gas phase was estimated to be 11.25 mg/m^3 corresponding to a water phase concentration of 75 μg/l. The properties of benzene as a toxic component in the leaked fuel oil were used in the model. The properties of the contaminated site soil and the contaminant's components are tabulated in Table 1. Fig. 2 shows the distribution of the contaminant as a function of vertical distance from the source to the water table. The distribution of the contaminant is calculated at a steady state condition and was compared to the field measured data. An acceptable agreement between measured and modeled data was observed.

4.2. Model Sensitivity Analysis

In more general terms, uncertainty and sensitivity analysis investigate the robustness of a study when the study includes some form of computational modeling. Predictions are highly dependent on the quantity and quality of space and time data. In this case a sensitivity analysis study was performed to evaluate the impact of various input parameters on soil contaminant level and loading to groundwater. A qualitative description of each parameter's sensitivity to the calculated groundwater impact and soil concentration profile is exhibited in the Tables 2 and 3.

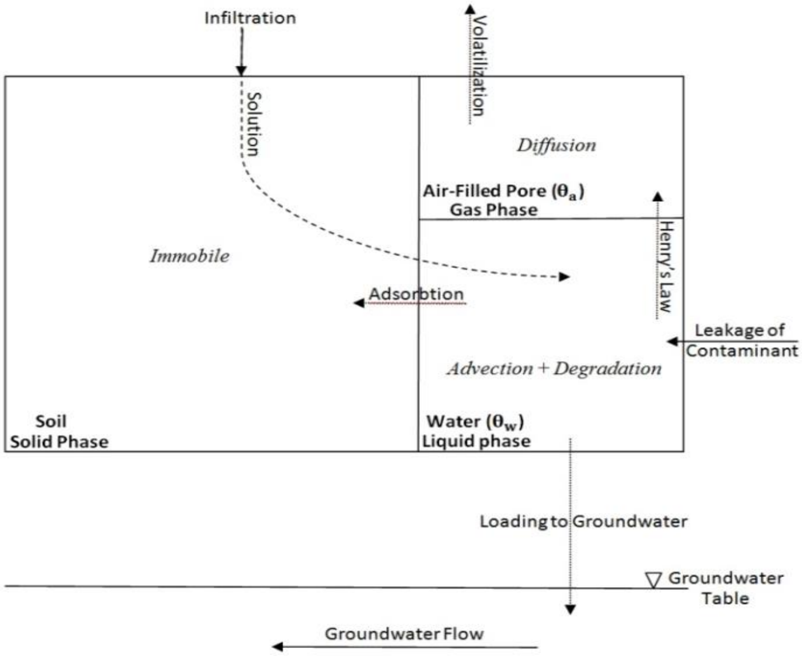

Fig. 1. Conceptual sketch of the most effective mechanisms considered in the simulation. In solid phase as an immobile phase: adsorption and solution adsorbed contaminant into the water pass through the soil, in liquid phase: advection, degradation and desorption into the gas phase and in outrance loading to groundwater, in gas phase: diffusion and volatilization to the atmosphere is considered.

Table 1. Model parameters data and chemical properties for benzene used for model validation [3]

q (mm/year)	Area (m^2)	WS^{*1} (mg/lit)	$C_{w,source}{}^{*2}$ ($\mu g/lit$)	H^{*3} (m)	λ (day^{-1})	Time (year)
200	25	1732	75	18 ^{b}	0.01	200
f_{oc} (-)	θ_t (-)	θ_w (-)	ρ_b (g/ml)	D_{air} (m^2/day)	K_H (-)	K_{oc} (ml/g)
0.02	0.45	0.15	1.7	0.76	0.15	22

*1: water solubility of benzene

*2: average source zone concentration in the water phase

*3: groundwater table below land surface

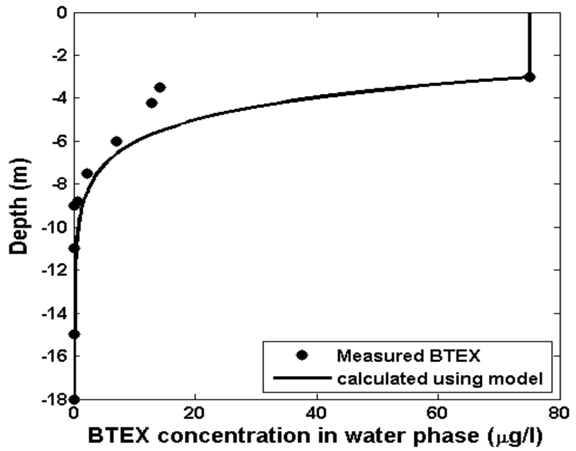

Fig. 2. The comparison of contaminant concentration in the unsaturated zone below the source is calculated using 1D numerical model (in solid line). The results are based on a constant source concentration in the water phase of 75 μg/l, which is the average of the measured concentrations within the source zone. Also shown are field measurements of total pore water BTEX concentrations below the source shown as (•).

4.3. Model Application in contaminated site

Fig. 3 shows the total contamination profile for one of the most contaminated drilled boreholes mainly due to the underground leakage. The current contamination level was used as an initial value in the model; then, prediction was made for spreading of the plume and loading to groundwater in the future years for four different scenarios. Not surprisingly, results obtained from GC-MS analysis showed that the soil contained numerous chemical compounds. Clearly, estimation of contaminant transport for each of these compounds was nearly impossible. To overcome to this difficulty, the contaminated soil was extracted by water and the total hydrocarbon content of solution was found 49.5 mg/lit. Consequently, all of the hydrocarbon compounds were considered as a single component with the above-mentioned solubility. This is helpful for a reliable risk assessment of plume and contaminant influx down to the groundwater. Soil properties such as bulk density, porosity, humidity and annual precipitation were taken from geotechnical studies performed in the area. The contaminant and soil properties are summarized in Table 4.

4.3.1. Different scenarios for predicting contaminant plume and loading to groundwater

On the way down to risk assessment goals, the model was applied in different cases by defining of different scenarios with two optimistic and pessimistic extremities based on the rate of bio-degradation and future rate of leakage. Comparing results obtained by different scenarios can be considered to make a suitable decision for site remediation and prevent further leakages. For each scenario the model was run for different upcoming years until the remained contaminant in the soil reached to the end. Four different scenarios are considered as follows:

4.3.1.1. First scenario-most optimistic state view

In this scenario it was assumed that there will be no contaminant leakage in the future, i.e., the source point behaves like a non-permanent source. Bio-degradation was also considered as an effective process. The bio-degradation rate for total hydrocarbons was assumed 0.01 day^{-1}. Results are shown for first scenario in Figs. 3 and 7.

4.3.1.2 Second Scenario- optimistic state

In this scenario it was assumed that there will be a continuous leakage of the contaminant for next 15 years (permanent source). Furthermore, in these 15 years it is assumed that there would be an increase of contaminant content by 5% each year in the higher part of the source, the first 6 meters of the source height. Similar to the first scenario, bio-degradation rate of 0.01 day^{-1} was considered as effective process in this scenario. Results are shown in
Figs. 4 and 7.

4.3.1.3 Third scenario-pessimistic state

Unlike the first and second scenarios, in this scenario it was assumed that biodegradation is not significant. Similar to the first scenario, the leakage has already been stopped and the source point behaves like a non-permanent source. Results are shown for this scenario in Figs. 5 and 8.

Table 2. Parameter sensitivity of model for soil concentration profile.

Parameters	Area	f_{oc}	q	θ_t	ρ_b	θ_w	D_{air}	K_H	K_{oc}	λ
High		×	×						×	×
Moderate				×	×	×				
Low	ineffective						×	×		

Table 3. Parameter sensitivity of model for mass loading to groundwater.

Parameters	Area	f_{oc}	q	θ_t	ρ_b	θ_w	D_{air}	K_H	K_{oc}	λ
High	×	×	×						×	×
Moderate						×				
Low				×	×		×	×		

4.3.1.4 Fourth scenario-most pessimistic state

In this scenario, source condition for the next 15 years is similar to the second scenario, but bio-degradation is not significant. Results are shown in Figs. 6 and 8.

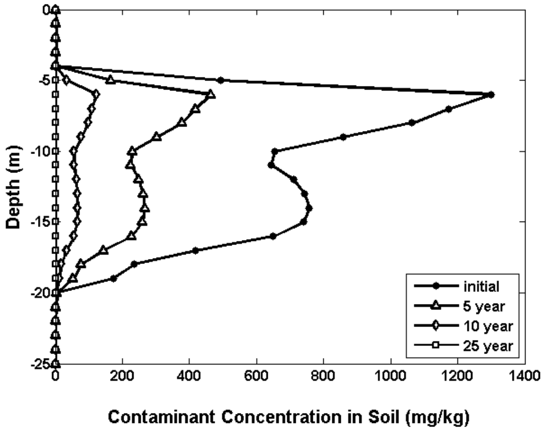

Fig. 3. Total soil contaminant profiles in different years-scenario 1. Also shown are profile of the total contamination in TOG (mg/Kg) in May 2010 located at phase 2&3 SPGC as an initial value.

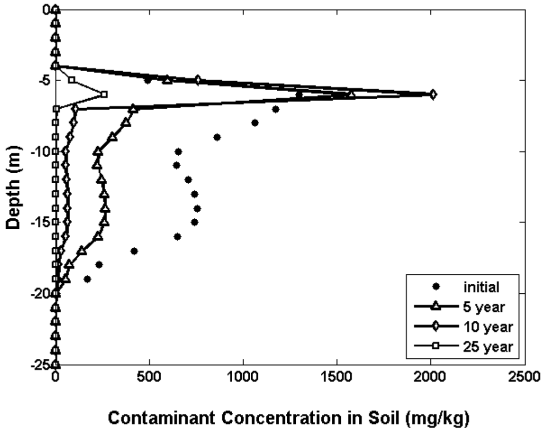

Fig. 4. Total soil contaminant profiles in different years-scenario 2.

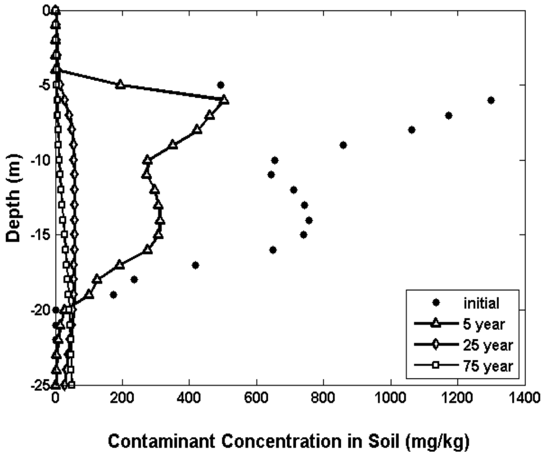

Fig. 5. Total soil contaminant profiles in different years-scenario 3.

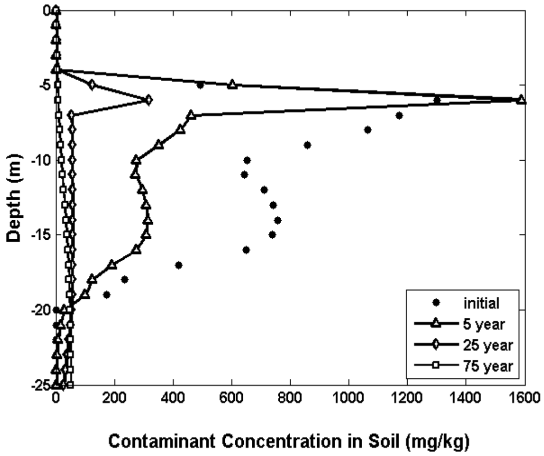

Fig. 6. Total soil contaminant profiles in different years-scenario 4.

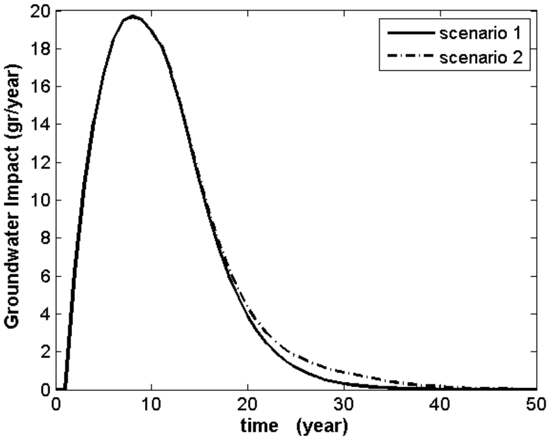

Fig. 7. Comparison of different mass loading to groundwater for scenarios 1 and 2.

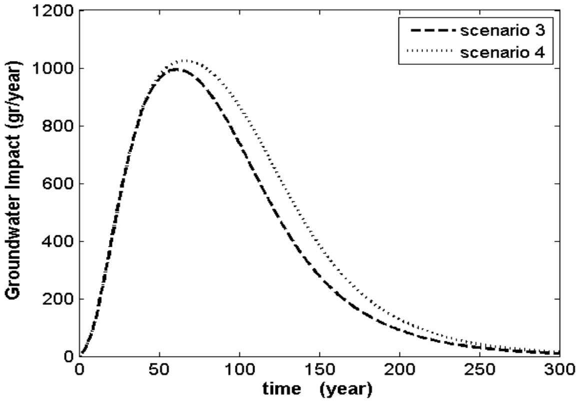

Fig. 8. Comparison of different mass loading to groundwater for scenarios 3 and 4.

5. Discussion

Numerous hydrocarbon compounds were identified in the GC-MS analysis. To avoid out of control complexity and to have a convenient model, all the hydrocarbons were considered as a lump component presented by TPH (mg/kg). Unlike the analytical solution models, it is possible to use the numerical model for heterogeneous soils. The model presented here is fortified in such a way that if the porosity profile, humidity, or infiltration of surface waters in different season is available, the model can predict the future situation. In the risk assessment of contaminated sites, according to the variation in the contaminant properties and polluted soil, the lack of accurate data used in modeling is considered normal. For this study, a reasonable range of each parameter respondent to local conditions and pollutants materials is considered [18]; and then, in this range, based on the sensitivity analysis, the minimum or maximum value is selected. The focus in this study was based on biodegradation. In the pre-defined scenarios, one of the most important factors considered in each scenario is the presence or absence of the bio-degradation mechanism as an effective process. First order bio-degradation is considered with the roughly low hydrocarbon decomposition rate of 0.01 day^{-1}. However, even this low rate bio-degradation indicates a very significant role in natural attenuation while the results of different scenarios are being compared. The results are shown in Figs. 3 and 4 for the first and second scenarios, respectively that included bio-degradation which shows faster attenuation in the contaminant profile in comparison with the results that are shown in Figs. 5 and 6 for third and fourth scenarios with no bio-degradation, respectively. Total period of mass flux of contaminant into groundwater table in Fig. 7 shows 40 and 50 years for the first and second scenarios respectively when the bio-degradation process was considered as an active process; on the other hand for the same conditions but without bio-degradation process the mass flux period of roughly 300 years as it is shown in Fig. 8 is obtained for the third and fourth scenarios showing that bio-degradation has a significant role on the contaminant attenuation. The contamination leakage may persist for the next 15 years (equivalent to the remaining effective life of the refinery) and 5% of the amount will be added each year; this is an idea that occurred in the second and fourth scenarios that represented poor environmental conservation policies in the plant. However in this case study, due to high contaminant leakage rate, additional contaminant leakage in upper layers has a less effective impact than bio-degradation on the soil concentration profile or the extent of contamination in the groundwater. This effect is more obvious when comparing Fig. 4 with Fig. 3 and Fig. 5 with Fig. 6. In the scenarios in which bio-degradation has been considered, the decomposition rate was assumed as a first order reaction. To be more accurate, a biological reaction rate follows the Monod kinetic model. However, when the substrate concentration is low, such as the concentration of this contaminant in the soil, the Monod equation can be approximated by first order reaction [19]. Using the presented model is plausible even when the biological processes are fortified. These kinds of fortification, especially done as in-situ processes, e.q., nutrient addition and humidity adjustment, increase the rate of degradation that can be considered in the model.

Table 4. Model parameters applied for contaminated site in our case study

q (m/year)	Area (m^2)	Aqs^{*2} (mg/l)	Δz (m)	H^{*1} (m)	Δt (year)	Time (year)
0.22[a]	100[b]	49.5	1	25[b]	1	variable
f_{oc} (-)	θ_t (-)	θ_w (-)	ρ_b (g/ml)	D_{air} (m^2/day)	K_H (-)	K_{oc} (ml/g)
0.003[d]	0.37[c]	0.23[c]	1.78[c]	0.8235[d]	0.10736[d]	163[d]

*1: groundwater table below land surface *2: average solubility of pollutants in water

References: a: South Pars special economic zone database, b: site visit & field sampling, c: geotechnical studies performed in the area, d: [18]

6. Conclusions

In this study, a one-dimensional multiphase vertical model is presented with the aim of being applicable to risk assessment of contaminated sites. After sensitive analysis and validation, the model was applied for a contaminated zone of a gas refinery plant. Different scenarios were considered to evaluate the associated risks. Based on the simulation results the following conclusions were made:

1. In this particular contaminated zone, leakage of contaminant has occurred on the nearby water surface and the groundwater contamination will occur in the near future.
2. Considering different scenarios, maximum groundwater impact was calculated as nearly 1000 g/year for the pessimistic view with no bio-degradation in effect and 20 g/year for the optimistic view including bio-degradation, and the extant time of the contaminant in an optimistic view was 50 years and for the pessimistic view was around 250 years.
3. Bio-degradation rate is found as a critical process for the contaminant attenuation in the unsaturated zone and reduction of contaminant loading to groundwater.

4. Bio-degradation considerably decreases the spread of contaminant down to groundwater, so by enhancing the bio-degradation rate with bio-stimulation of the contaminated soil, the chance of groundwater contamination could be reduced.

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