Model for simulation of movement and biodegradation of hydrocarbons in saturated and unsaturated soils

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Abstract

A numerical model was developed and validated, to describe the processes governing the flow, transport and biodegradation of hydrocarbon spills in aquifers, using the Cholesky method. Model simulations showed good correlation with available experimental data for each individual process. The model was used to evaluate the efficiency of direct oxygen and bacteria injection into the aquifer as a bioremediation method for a fuel hydrocarbon spill case.

1 Introduction

Pollution of aquifers by hydrocarbons involves both the vadose and saturated zones, where various processes, including phase movement and chemical and biological reactions take place. These biological reactions constitute a good possible tool to clean or slow the advance of contaminant plumes if properly applied.

This article presents a two dimensional numeric model that simulates the behaviour of a LNAPL (Light non-aqueous phase liquid) hydrocarbon spill, taking into consideration all the previously mentioned processes. This includes phase movement for water and hydrocarbon, mass transfers between these phases, solute transport in the water phase and aerobic or anaerobic biodegradation kinetics.

The model has been validated using experimental results from several literature sources and used to simulate the effect of the direct injection of oxygen and microorganisms to a fuel contaminated aquifer.
2 Solute flow and transport model

The proposed model, is controlled by the following phenomena: (1) Liquid phase flow, dependent on the phase and soil characteristics; (2) Mass exchanges between the different solutes, phases and soil components; (3) Solute transport through the liquid phase, which depends on fluid and contaminant characteristics and (4) Biodegradation kinetics, dependent on the characteristics of the contaminant and of microorganisms present.

2.1 Phase flow equation

The general equation used to describe groundwater flow is the Richards [1] equation expressed as:

\[ C(h^a) \frac{dH^a}{dt} = \frac{d}{dx} \left( K^a \frac{dH^a}{dx} \right) + \frac{d}{dz} \left( K^a \frac{dH^a}{dz} \right) \]  

(1)

where \( H^a \) is the hydraulic head (L), \( K^a \) is the hydraulic conductivity (L/T) and \( C(h^a) \) is the soil capillary capacity (L/L) of the liquid phase \( \alpha \).

The hydraulic conductivity for each phase \( \alpha \) is a function of the water content, and it is defined as:

\[ K = K_{r\alpha} K_{\text{int}} \frac{\rho_a g}{\mu_a} \]  

(2)

where \( K_{r\alpha} \) is the phase relative conductivity, \( K_{\text{int}} \) is the soil intrinsic conductivity (L/T), \( \rho_a \) is the phase density (M/L^3), \( \mu_a \) is the phase dynamic viscosity (F*T/L^2) and \( g \) is the gravity constant (L/T^2).

The relative conductivity can be expressed by the Van Genuchten's [2] equation, modified for the water and hydrocarbon cases as:

\[ K_{r\alpha} = \left( \frac{\theta_w}{\theta_s} \right)^{2+3\lambda \over \lambda} \]  

(3)

\[ K'_{r\alpha} = \left( \frac{\theta_w}{\theta_s} \right)^2 \left( \frac{\theta_w + \theta_o}{\theta_s} \right)^{2+3\lambda \over \lambda} - \left( \frac{\theta_w}{\theta_s} \right)^{2+3\lambda \over \lambda} \]  

(4)

where \( \theta_w \) is the water content (L^3/L^3), \( \theta_o \) is the hydrocarbon content (L^3/L^3), \( \theta_s \) is the saturation water content (L^3/L^3) and \( \lambda \) is the pore size distribution index.
Equation 4 assumes that hydrocarbon flow occurs through the available space in the soil pores, and thus, considers water as a frozen phase not displaced by the others.

2.2 Mass exchange

Two ways of mass transfer are considered in this model: volatilisation and dissolution. The equation for volatilisation is the Raoult\[3\] equation given by:

\[
H_{ah} = \frac{P_m P}{RT}
\]

where \(H_{ah}\) is the gaseous partition coefficient for the component \((M/L^3)/(M/L^3)\), \(P_m\) is the molecular weight \((M/mol)\), \(P\) is the vapour pressure for the component \((P)\) and \(R\) is the universal gas constant.

The equation for dissolution is given by Corapcioglu \& Baehr [4]:

\[
C_w = H_{wh} X_h \gamma
\]

where \(C_w\) is the component concentration \((M/L^3)\), \(H_{wh}\) is the liquid partition coefficient for the component \((M/L^3)/(M/L^3)\) and \(\gamma\) is the activity factor.

2.3 Solute transport

The transport of a contaminant in a soil, can be modelled by the advection-diffusion equation [5] given by:

\[
\frac{\partial}{\partial t} (C_k) = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial C_k}{\partial x_j} \right) - \nu_i \frac{\partial}{\partial x_i} (C_k) + \Phi_k + A_k
\]

where \(C_k\) is the solute concentration and \(D_{ij}\) is the dispersion tensor \((L^2/T)\) (includes Dispersion and Diffusion), \(\nu_i\) is the average pore velocity \((L/T)\), \(\Phi_k\) is the consumption rate for solute \(k\) and \(A_k\) is the sources and sinks for solute \(k\).

2.4 Biodegradation kinetics

The effect of biodegradation on the contaminant, is described by Monod’s equations. Aerobic and anaerobic processes are both taken in consideration, using oxygen or nitrogen as electron acceptors in each case. The system of equations [6] can be written as:
where $A$ is the electron acceptor concentration (M/L$^3$), $C$ is the hydrocarbon concentration (M/L$^3$), $M$ is the microorganisms concentration (M/L$^3$), $k$ is the maximum substrate utilization (l/T), $K_c$ is the substrate saturation coefficient (M/L$^3$), $K_a$ is the electron acceptor saturation coefficient (M/L$^3$), $F$ is the electron acceptor use rate (M/M), $Y$ is the microorganisms yield rate (M/M), $b$ is the microorganisms decay rate (1/T).

2.5 Dominion definition

The solution is implemented in a dominion defined as a bi-dimensional grid of rectangular cells in the x,z plane (Fig. 1). At the bottom, impermeable border conditions are imposed, while at the top inflow border conditions for water and/or hydrocarbon are implemented. At both sides of the dominion, there are water trenches with a given water height. This water level defines the hydraulic head at each of the borders.

![Figure 1: Domain characteristics](image)

2.6 Numerical solution

Given the complexity of the problem, the processes are applied in a sequential manner throughout the dominion and the equations are solved in the following
order: (1) Phase flow calculations; (2) Solutes transport; (3) Mass exchange between phases; and (4) biodegradation. Each of these processes is solved with a different numerical procedure: for phase flow, an implicit matrix solution method is proposed using an adaptation of the Cholesky algorithm, with various optimisations for the use of memory and speed in a personal computer; the three other processes are solved in an explicit way, cell by cell, using one or a system of equations.

To control the behaviour and convergence of the model, several mathematical considerations were included in the computer code, but most importantly, the Peclet, Newmann and Cell size criteria [7] were implemented in each step of the simulation.

3 Model validation

3.1 Water and hydrocarbon flow validation

The model was validated for all its processes, using literature examples. Phase flow for water was validated using the work of Khanji [8]. The simulation of the advance of the infiltration front bears an excellent correlation with his results as seen in figure 2.a. One dimensional Hydrocarbon flow validation was done by comparison with the results of Sunada and Eckberg [9] experiences. His results are also satisfactorily simulated (Fig. 2.b). Two dimensional flow for hydrocarbon was validated with an experimental setup based on a previous experience by Van Geel & de Sykes [10]. The modelled oil bulb matched the shape of the experimental oil border at the end of the simulation. (Fig. 2.c)
3.2 Solute Transport and Biodegradation validation

For solute transport and biodegradation, the study into natural bioremediation of Abriola (1997) was explored. This work provides the evolution and biodegradation of a plume of toluene, which was recreated as accurately as possible in the model by the use of several stimulus and initial conditions. After the simulation, the results were compared to the field data provided by Abriola [11] (Fig.3). Although different in some respects, the correlation between the simulation (contour lines) and field data (points), was good enough to validate the model.

4 Application to a hypothetical case

4.1 Case description

A hypothetical case of hydrocarbon spill was devised to test the biodegradation simulation capabilities of the model, under different conditions. An area of 55 meters long and 15 meters depth was created, with a water table at 10 and 6
meters below the surface at the right and left sides of the dominion respectively. The soil was defined with a hydraulic conductivity of 40 m/d.

A spill of 5 cm/hr was injected, in a length of 1 meter, at 10 meters from the left border. The spill consisted of a generic hydrocarbon with a viscosity of 0.0005 N*s/m² and a density of 0.8 gr/cm³. The component of the hydrocarbon monitored is toluene. The spill was maintained for a period of 2 day. The model was run for a simulation time of 60 days, with a maximum time step of 0.5 hours and an initial vertical cell size of 1 meter. The state of the system, and the size and shape of the contaminant plume without biodegradation after 1 month is presented in Fig. 4.

![Figure 4: Hydrocarbon content and concentration after 30 days.](image)

**4.2 Biodegradation analysis with the model**

Given the characteristics of the case, different conditions of biodegradation were applied to the contaminant plume. First, natural biodegradation using the microorganisms present in the soil for 60 days (Fig. 5). This was compared with a forced biodegradation by injection, with a flow of 1 cm/hr, in 4 points (fig. 6) of a solution rich in bacteria and oxygen for different periods of time, 30 days after the start of the simulation. This solution was composed of water with 1e-05 gr/cm³ of oxygen and 1.8e-5 gr/cm³ of microorganisms, well above the natural standard. A Comparison was done increasing and decreasing both injection times and microorganisms concentration.
From comparison with figure 5, figure 6 shows a smaller toluene plume when applying the surface injection of the microorganisms solution. The mass removed from the plume in the saturated zone only, amounts to 10%. The process itself is very slow, taking one month to remove this quantity, for an injection period of one week with a concentration of 1.5e-05 grs/cm³ of bacteria. The relation between injection time or concentration and percent of removal is almost linear at this concentration and simulation time ranges. Given the bacterial decay rate, it can be predicted that 2 to 3 years would be needed to bioremediate the contaminant plume.

5 Conclusions

The model has been validated to a good degree of accuracy through the various independent tests for each process. Although no extensive experimental
Results obtained from the model, show that the biodegradation process is indeed effective in removing the dissolved hydrocarbon and thus slow the advance of the contaminant plume. The process itself is very time consuming, making it viable only for small scale, low concentration pollution events. For other cases, it is possible to apply this method, but it would be very expensive and time consuming. Other methods, like bio-reactive barriers, would be better suited to this end.

6 References


