

An industrial 3-D numerical model for simulating organic pollutants migration and site remediation

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Abstract

This paper presents a general numerical model able to simulate both organic pollutants migration (3-phase compositional flows, mass transfer, transport) in soils and aquifers and decontamination techniques such as pumping, in situ stripping, venting, hot venting, steam injection, surfactant injection and biodegradation.

To validate the simulator, a 3-D experiment in a large pilot was carried out. A total of 475 liters of diesel oil was injected in the pilot and numerous in-situ measurements were performed to determine pollutants location and concentrations within the vadose and saturated zones. Prior to the pilot test, a predictive run computed the extent of the contaminated zone and the oil saturations. Numerical results showed good agreement between experiment and simulation.

To demonstrate the simulator abilities in modeling field cases, two examples are given with comparison with on-site observations: (1) soluble hydrocarbon transfer and transport at regional scale; (2) free-oil pumping.

1 Introduction

Among the hazards for soil and aquifer pollution, the infiltration of hydrocarbons and chlorinated solvents represents one of the most serious threats. This infiltration resulting from accidental spills during production, transport or storage of these compounds can deteriorate underground water quality for long periods of time. Contamination by a nonaqueous phase liquid (NAPL) remains a complex problem. Understanding the evolution of NAPL in soils and aquifers requires knowledge of various phenomena:

- vertical migration of NAPL from surface to water table, then spreading in the capillary fringe and creating a contaminated zone at residual oil saturation;
- evaporation of volatile compounds creating a gaseous envelope of oil vapor;

- dissolution and transport of soluble compounds in water phase leading to a "plume" of contaminated water in the aquifer;
- interactions between pollutants and the porous matrix (adsorption);
- natural biodegradation of both dissolved pollutants and residual NAPL trapped in the pores.

Good comprehension of the above mechanisms can be obtained with the help of numerical simulators as reviewed by Pinder and Abriola [1], Corapcioglu and Panday [2] and Panday et al. [3].

Numerical models aim also at simulating decontamination processes such as pumping, air stripping, venting, steam injection, biodegradation, surfactant injection, ... While these various methods have been studied at the laboratory scale and have been used in field conditions, the design of an operation is often empirical. Use of a comprehensive simulator may significantly increase our knowledge about the complex phenomena associated with the above mentioned processes and our capability in optimizing such reclamation operations.

The purpose of the present study is to describe a general simulator, SIMUSCOPP, able to simulate most of the organic pollutants (hydrocarbons, chlorinated solvents) behavior and remediation processes discussed above. Then, 3 cases are presented to compare computed results and observations: (1) migration of diesel oil into a large-scale basin, (2) description of an accidental spill of gasoline 30 years ago, transfer of soluble products within the aquifer and transport at regional scale, and (3) site remediation by free-gasoline pumping.

2 Model description

The SIMUSCOPP model is a general 3-D simulator, dedicated to pollution/remediation problems, able to simulate most of the phenomena and remediation techniques listed above, including biodegradation, steam injection and surfactant injection. It solves problems of 1, 2 or 3-phase flow, compositional or not, from the laboratory scale to the site scale. Geometry can be described by cartesian coordinates or radial coordinates, with possible local mesh refinement. Its code is portable between most common computers: PC, Unix workstations and also vector computers.

The mathematical description of compositional multiphase flow in porous media is based on equation of mass conservation for each component and momentum conservation for each phase. The general mass conservation equation for a component i existing in the three fluid phases (p) and adsorbed on the matrix (r) is:

$$\frac{\partial}{\partial t} \left[\phi \left(\sum_{p=1}^{N_p} \rho_p \cdot S_p \cdot x_i^p \right) + (1 - \phi) \cdot \rho_r \cdot q_i^r \right] + Q_i + R_i + \text{div} \left(\sum_{p=1}^{N_p} \rho_p \cdot x_i^p \cdot \alpha_i^p \cdot \vec{u}_p + \vec{J}_i^p \right) = 0 \quad (1)$$

In this equation the flux modifiers, α_i^p , have been introduced to limit transfer between phases. They have been tested in a previous study to describe nonequilibrium dissolution of hydrocarbon in water [4].

The momentum equation for each fluid phase is reduced to Darcy's generalized law.

In order to close the system of equations, constitutive equations must be written for phase densities and viscosities, equilibrium partition constants, molecular diffusion and hydrodynamic dispersion, adsorption and biodegradation rates for both dissolved and residual organic products. These various relationships are not described in the present paper.

3. Diesel oil migration into a large-scale basin

The simulation results discussed here were performed by simulating 3-D diesel oil infiltration on a pilot scale. This pilot (SCERES basin), located at the CNRS-Campus of Strasbourg (France), is a large impervious concrete basin (25 m long x 12 m wide x 4 m deep) packed with quartz sand. The porosity of the sand is 40%, and its hydraulic conductivity is $8 \cdot 10^{-4}$ m/s (intrinsic permeability = 80 darcy). This pilot was built to test some decontamination processes such as surfactant-aided recovery and in-situ bioremediation [5,6]. During the summer of 1994, the basin was contaminated with 475 liters of diesel oil through a limited area of 1.8 m^2 , 3 m above the water table. After a few months of stabilization, core-drill investigations were performed in order to determine the shape and extent of the residual contaminated zone and pollutant concentrations (i.e., oil-phase saturations) in the various parts of this contaminated zone. The diameter of the oil-impregnation body in the unsaturated zone was about 1.85 m. The horizontal extent of the oil phase in the capillary fringe was in the range of 5.60 m to 5.90 m, with a mean thickness of 10 to 15 cm. Residual oil saturations were close to 5% of pore volume in the unsaturated zone and in the range of 21 to 24% in the capillary fringe [7].

In a second stage, an elevation of 0.5 m of the water table was performed in order to vertically displace the oil phase initially trapped in the capillary fringe. New measurements gave a value of 10% for the residual oil saturation in the saturated zone after the rise of the water table.

The purpose of this numerical modeling was to reproduce the migration of diesel oil in the SCERES basin and the shape and final extent of the contamination. For this, we performed runs with three-phase non-compositional flow. Only three components were taken into account: oil, water and air, without any mass transfer. The SCERES basin was discretized with 12000 grid-blocks (25 x 24 x 20). Three-phase relative permeabilities for the oil, water and air phases were obtained by laboratory experiments. The water-air capillary pressure curve was obtained by inversion of the vertical water saturation profile measured in the basin by a neutron probe before the oil spill. Water-oil and air-oil capillary pressure curves were then obtained by scaling the water-air curve according to their respective interfacial tensions. The main data used for the runs are given in Table 1. Four boundary conditions were used for this run:

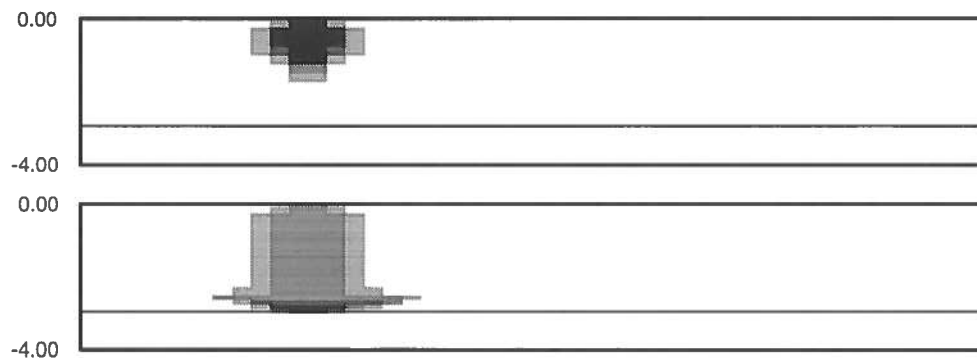
1. aquifer influx: pressure in the water phase was fixed at 1 atmosphere at the top of the water level, and water was injected between -3 and -4 m;
2. aquifer outflux: pressure was fixed at 1 atmosphere at -3.125 m, corresponding to the slope of the water table (5‰), and water was produced between -3.125 and -4 m;
3. pollution infiltration: area at the top of the model ($z = 0$) where diesel oil was injected at a constant rate of 9 liters per minute (475 liters injected);

4. surface of the model: pressure in the gas phase was fixed at 1 atmosphere, allowing air to get out of the system when oil was infiltrating.

oil density	= 838 kg/m ³
oil viscosity	= 3.91 mPa.s
irreducible water saturation	= 0.2
residual oil saturation (air-oil flow)	= 0.05
residual oil saturation (water-oil flow)	= 0.1
max. air-water capillary pressure	= 5000 Pa
max. water-oil capillary pressure	= 1700 Pa
max. air-oil capillary pressure	= 1200 Pa

Table 1. - Data for SCERES basin simulation

Figure 1 gives the shape of the contaminated zone and the oil saturations on a cross-section for two times: at the end of the diesel-oil injection (1 hour), and 2 months later, and an areal view at the top of the water table after 2 months. As shown in Fig. 1, the horizontal extent of the oil lens calculated by the simulator is close to 5.50 m, which is in very good agreement with the value observed. Regarding the oil spreading in the unsaturated zone, the calculated extent of the contamination is greater than the observed one. As shown in Fig. 1, The main cylinder of residual oil centered under the injection zone has a diameter of 2 m, which is in good agreement with the observations. Oil saturation in this zone is 5%. Around this main cylinder, the numerical model computed very low oil saturations, which have not been observed in the pilot. This is probably due to numerical dispersion in this zone or to excessive air-oil capillary forces leading to a lateral spreading of the contamination zone. Fig. 2 gives the vertical profile of oil saturations under the surface of pollution injection after 1 hour (end of injection), after 2 months and after the 0.5 m rise of the water table. As shown in Fig. 2, injected diesel-oil migrated vertically through the unsaturated zone and spread within the water-air capillary fringe. A vertical equilibrium was then reached, where the maximum of oil saturation was 28% (an average value of 24% was measured in the basin). The rise of the water table displaced this oil lens vertically and trapped the pollutant at its residual saturation of 10%. Calculated saturation profiles before and after the rise of the water table effectively reproduce the observations of the pilot.



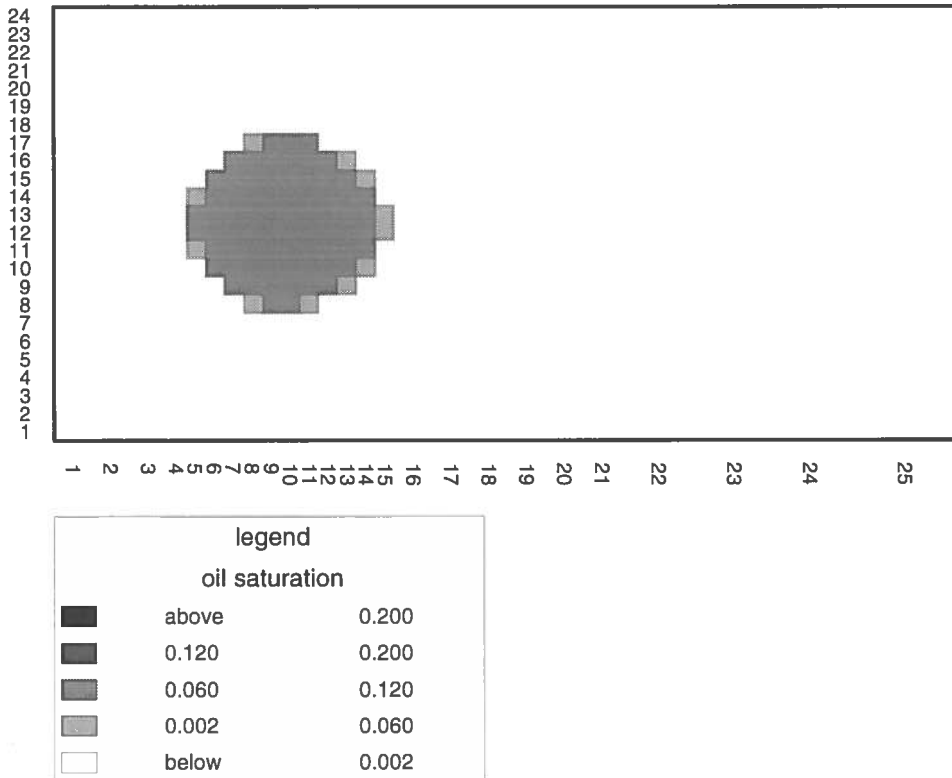


Figure 1: Oil saturations in the SCERES basin

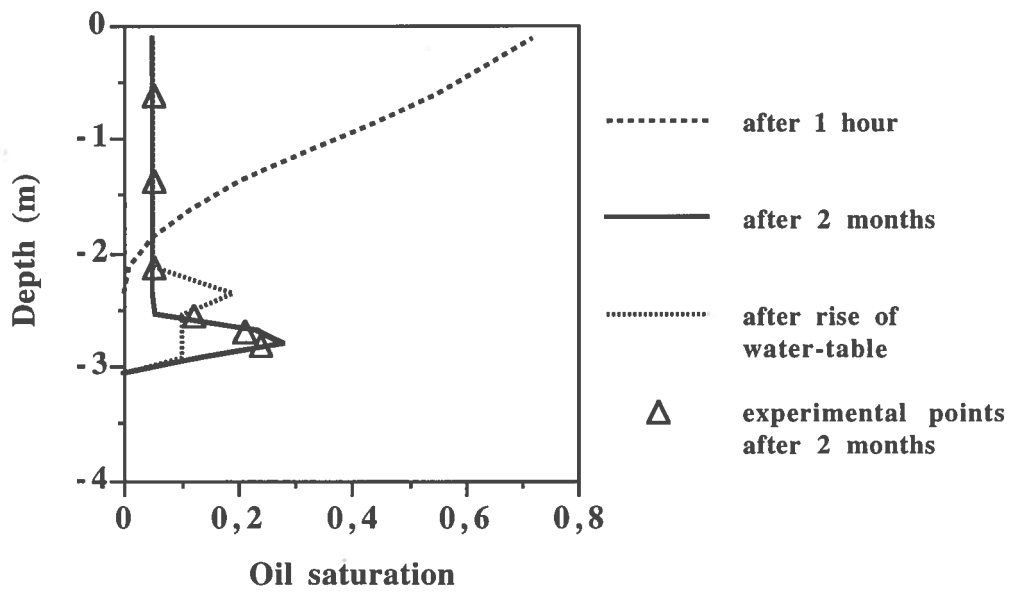


Figure 2: Computed oil saturations in the SCERES basin

4. Site 1: transfer and transport at regional scale

The simulation results given here concern a site of hydrocarbon storage contaminated by gasoline. The spill of gasoline occurred in 1963 and the volume

of infiltration was not known. A diagnosis of the site was carried out in 1994 to locate the residual contamination under this storage area and to measure the concentration of dissolved hydrocarbon present in various pumping wells located near the storage area. A first run was performed to calibrate the piezometry on the aquifer, taking into account bounding rivers, rain and water-pumping wells. Then, knowing the regional flow and more precisely the direction of the aquifer flow under the storage area, a second set of runs was done in order to describe the spill of gasoline. Several scenarios were built with spill volumes ranging between 1 m³ to 100 m³ of gasoline. The comparison between simulations and on-site observations demonstrated that the spill that occurred in 1963 could be close to 15 m³. In this latter case the computed extent of the residual contamination was compatible with the observed one. Moreover, analyses performed in 1994 on the pollutants showed clearly that the initial product have been slightly modified during 30 years: minor dissolution of aromatics and no significant biodegradation and vaporization. Knowing approximately the volume of gasoline infiltrated, a third set of runs were carried out to describe the dissolution of aromatics and their transport at large scale in the aquifer. Measurements carried out in 1994 showed that the water under the storage area contained 15 ppm of BTEX (benzene, toluene, ethylbenzene, xylene). In an observation well located 2 km downstream the storage, hydrocarbon concentrations in water were between 20 to 50 ppb.

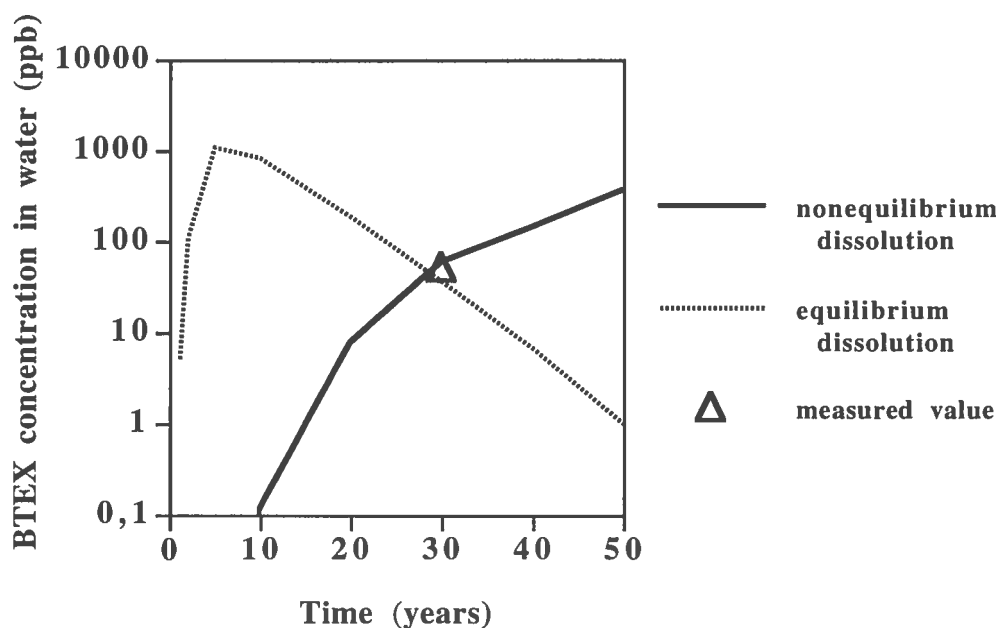


Figure 3: Computed BTEX concentrations in the aquifer under the storage

A first calculation assumed thermodynamical equilibrium for dissolution. As shown in Fig. 3, the computed BTEX concentration in the observation well after 30 years is in good agreement with the value observed, but concentrations under the storage (Fig. 4) are close to zero, which is not compatible with the 15 ppm observed in 1994. In order to limit the transfer of hydrocarbon from the residual oil to the aquifer, a second run was carried out, using flow limitors which allow to reproduce nonequilibrium dissolution effects [4]. A calibration run was then

performed to reproduce both the concentrations under the storage and in the observation well, as shown in Figs. 3 and 4. Then, the calculation was extended in order to forecast the evolution of contaminant transport in the aquifer for the next 20 years. Simulation results obtained with the nonequilibrium assumption show clearly that BTEX concentrations in water are still increasing and that the aquifer will be contaminated for long time.

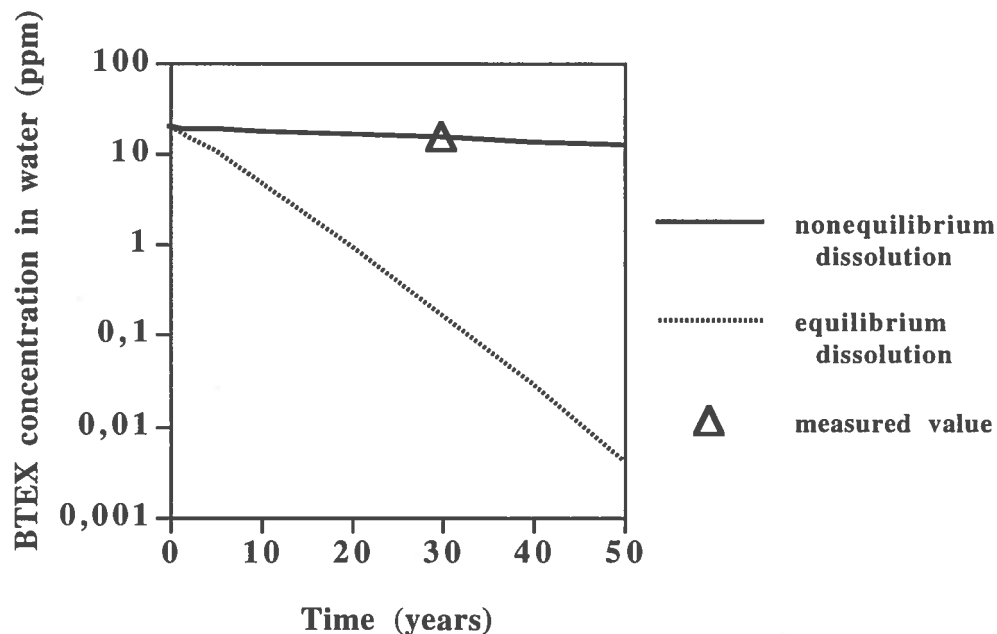


Figure 4: Computed BTEX concentrations in the aquifer under the storage

These results show the importance of taking into account nonequilibrium dissolution of hydrocarbon in simulations to ensure predictive calculations of pollutants propagation within the aquifer. The dissolution rates can be obtained by history matching and calibration of the model. After that phase, long-term forecasts can be handled.

5 Site 2: remediation by free-oil pumping

This last case consists of a site located in San Diego's area (California) where a layer of free-phase hydrocarbon was discovered in the groundwater, 15 to 18 feet below the ground surface. A pilot was then implemented on the site in order to recover the free-phase hydrocarbon by pumping groundwater together with the oil phase. Simulation discussed here describes a 30-day pumping test of one of the pilot wells. The porous medium consists of a sand with 10^{-3} m/s of hydraulic conductivity, polluted by gasoline. Three-phase relative permeabilities and capillary pressures were obtained via the Van Genuchten parameters measured on sand samples. Simulation were performed with a 2-D (rz) radial grid with 19 layers describing the unsaturated zone, the oil zone above the water table (thickness 2.9 ft) and the aquifer. The well test performed on-site can be summarized as follows: 15 days of water pumping at 1440 US gallon/day, 8 days at 2160 gallon/day and 7 days at 2880 gallon/day. Figs. 5 and 6 show the comparison between observation and calculation for two parameters: oil

recovery rate and drawdowns. These results show fair agreement between observed and computed results.

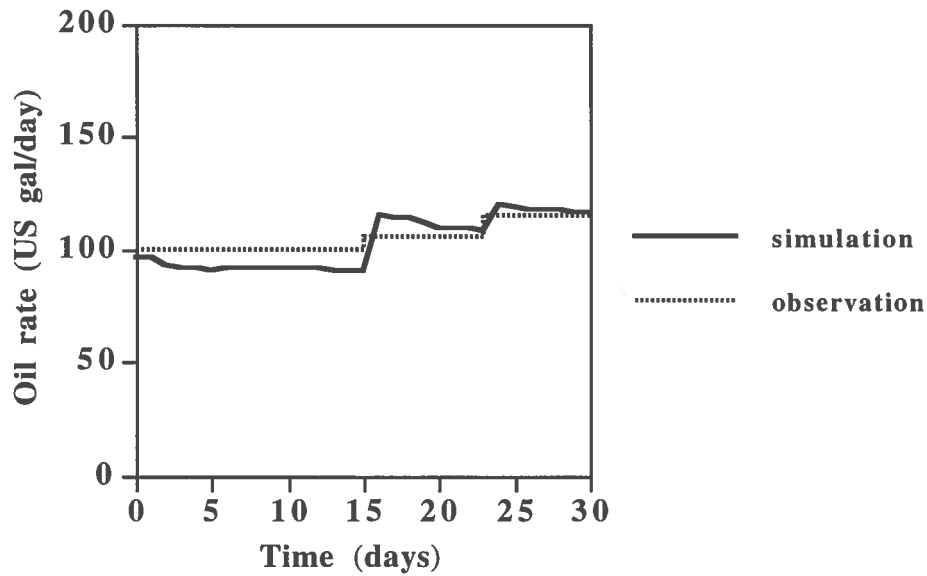


Figure 5: Comparison between observed and computed gasoline recoveries

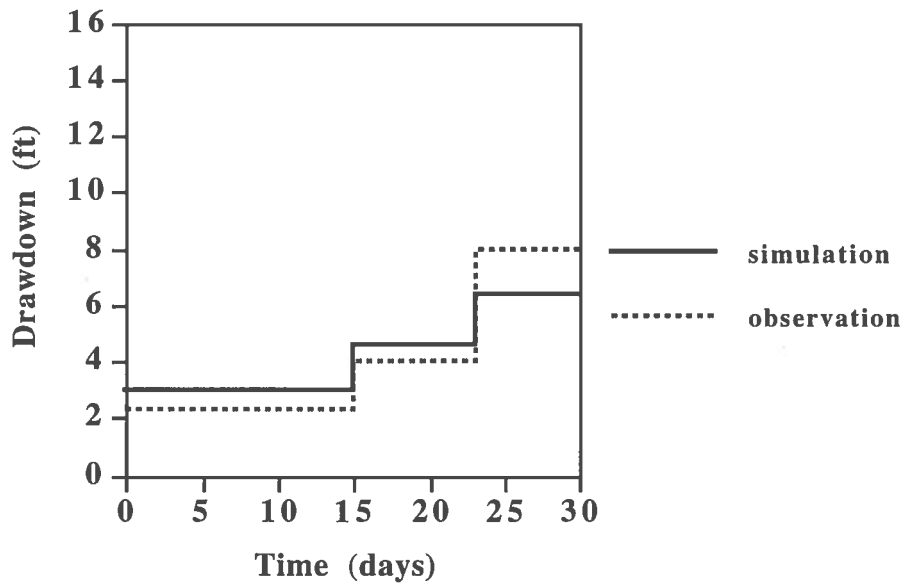


Figure 6: Comparison between observed and computed drawdowns

6 Conclusions

A general numerical model was developed to simulate organic pollutants migration in soils and aquifers, and most in-situ remediation techniques such as pumping, stripping, venting, hot venting, steam injection, surfactant injection and biodegradation. Three cases were simulated here, describing some of the various aspects encountered in pollution/remediation problems: (1) diesel-oil migration at pilot scale by means of three-phase flow in saturated and unsaturated zones, (2) dissolution of hydrocarbon under nonequilibrium

conditions and transport in the aquifer, and (3) free-oil recovery by water pumping on a site contaminated by gasoline. A good agreement between simulated results and observations was obtained for the three cases. This study shows that the SIMUSCOPP model can be an efficient and useful tool, capable of handling complex problems of risk assessment and remediation of sites contaminated by organic pollutants.

Nomenclature

\bar{j}_i^p	diffusion-dispersion flow of i in phase p , mol/s
P	phase pressure, Pa
q_i^r	mole fraction of i adsorbed on the solid phase
Q_i	component i injection/production source term, mol/s
R_i	component i biodegradation source term, mol/s
S_p	phase p saturation
t	time
\bar{u}_p	darcy velocity of phase p , m/s
x_i^p	molar fraction of i in phase p
α_i^p	flux modifier of i in phase p
ϕ	porosity
ρ_p	phase p molar density, mol/m ³

Subscripts

g	gas phase
i	component
o	oil phase
p	fluid phase (g, o, w)
r	rock phase
w	water phase

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