

Modelling Coupled Reactive Transport of PAH and Surfactants

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Abstract Within the framework of a comprehensive investigation concerning the use of surfactants to enhance the in-situ remediation of PAH contaminations in the subsurface, SMART, a multicomponent transport model, was developed to study the processes (interactions) taking place when surfactants and PAH migrate through porous media as solutes. The model is an adaption of a Lagrangian method allowing for separate treatment of conservative transport and reactive processes. It accounts for the hydraulic as well as for the physico-chemical heterogeneity of porous aquifers. The system of processes implemented in the model has been proven to be able to represent the behaviour of PAH and surfactants in porous media at the laboratory scale [Finkel et al., 1997]. Here, the transport model is applied to a simplified two-dimensional remediation scenario (field scale). It is shown how surfactants may influence the clean-up of PAH-contaminated aquifers. Emphasis is put on the effect of hydraulic and physico-chemical aquifer properties on the coupled transport of PAH and surfactants.

1. INTRODUCTION

The emission of polycyclic aromatic hydrocarbons (PAH) from coal tar contaminated sites such as former gas works endangers the quality of groundwater due to the high toxic, carcinogenic and mutagenic potential of the PAH. Since the highly hydrophobic PAH have low water solubilities, conventional remediation techniques such as pump-and-treat are not suitable for clean up of these sites within reasonable periods of time. Several investigations on the use of surface active agents (surfactants) to clean-up soils at the laboratory scale [e.g. Danzer and Grathwohl, 1997; Grimberg et al., 1995; Edwards et al., 1994; Burris and Antworth, 1992] as well as some field demonstration projects [e.g. U.S. Environmental Protection Agency, 1995] indicate that surfactants may influence the transport of PAH and thus are expected to enhance the remediation of PAH-contaminated sites. The enhancement can be achieved in three ways. Firstly, surfactants are able to reduce interfacial tension between water and nonaqueous phase liquids (NAPL) leading to an increasing PAH mobility (mobilization of entrapped residual phase). Secondly, surfactants may enhance microbial degradation rates. A third possibility is to influence the solubility of PAH.

The overall scope of this study is to identify and to quantify the governing processes involved in coupled transport of PAH and surfactants as solutes and, based upon that, to develop a transport model capable of predicting transport of PAH and surfactants in physically and chemically heterogeneous aquifer material. A modelling approach for simulating transport of PAH and surfactants at the laboratory scale has been presented by Finkel et al. [1997]. This paper presents some investigations on a simplified but typical two-dimensional scenario occurring with the remediation of PAH-contaminated sites by employing surfactants. In particular, it is demonstrated how large-scale hydraulic and physico-chemical heterogeneities may affect PAH and surfactant transport at the field scale.

2. REACTIVE TRANSPORT MODEL

2.1 Lagrangian approach

The transport model used here is based upon an approach of Dagan and Cvetkovic [1996], who presented a Lagrangian concept allowing for a separate treatment of conservative transport and reactive processes. In accordance with this concept conservative transport is quantified with respect to the travel time τ of an inert tracer. This leads to a probability density function (pdf) of travel time $g(\tau, x)$ for the transport of a conservative solute between an injection plane and a control plane which are a distance x apart from each other and are both oriented normal to the mean flow (Fig. 1). The pdf includes all information on hydraulic heterogeneity of the aquifer area considered. $g(\tau, x)$ may be directly measured during a tracer experiment or determined by simulation of groundwater flow and conservative transport employing appropriate analytical or numerical models.

Dagan and Cvetkovic [1996] presented analytical solutions for reactive transport for flow fields of uniform mean velocity. A radially convergent flow pattern is studied by Berglund and Cvetkovic [1995] in order to investigate some simple remediation scenarios. Here, non-planar injection and control surfaces perpendicular to the mean flow direction are introduced to account for non-uniform velocity fields. Some examples are given in Fig. 2. In a double well system the well screens may be taken (Fig. 2a). In the case of an extraction well in a uniform flow field the screen of the extraction well could serve as the control surface while a part of any isosurface of hydraulic head within the capture zone may be defined as the injection surface (Fig. 2b). For a funnel-and-gate system the cross-section of the gate (reactor) is a possible choice for both the injection and the control surface (Fig. 2c). It is obvious that these scenarios generally cannot be treated by analytical approaches but some numerical method has to be applied.

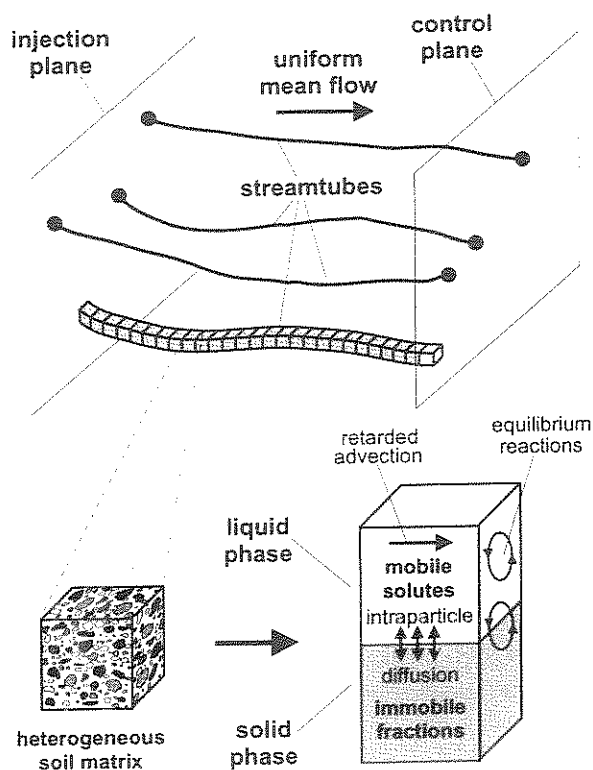


Figure 1: General scheme of the conceptual transport model: the heterogeneous flow field between an injection plane and a control plane is represented by an ensemble of streamtubes

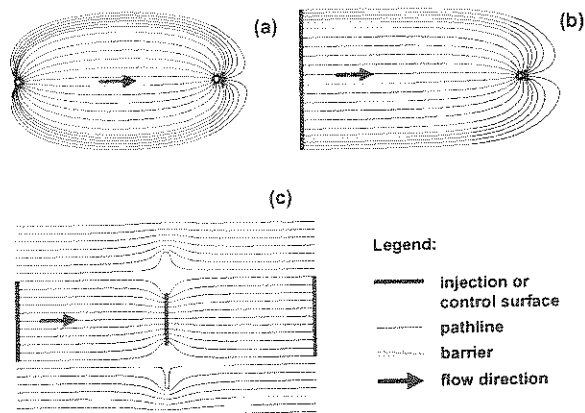


Figure 2: Examples (two-dimensional) for the definition of injection and control surfaces

2.2 Reactive Processes

Dagan and Cvetkovic [1996] describe reactive transport not with respect to spatial coordinates but with respect to the travel time τ of inert solutes. Following this approach a so-called reaction function $\Gamma(\tau, t)$ can be obtained. For any fixed time t this function represents a normalized concentration profile (Fig. 3) where $\Gamma(\tau, t)$ refers to all positions within the streamtubes that have been reached by a conservative tracer after a travel time τ . If physico-chemical parameters were homogeneously distributed or the scale of physico-chemical heterogeneity was considerably smaller than the transport distance it would be sufficient to deter-

mine Γ for a single streamtube which is in these cases 'representative' for all particles with respect to the reactions they are undergoing. In case of large-scale heterogeneities, however, Γ has to be determined separately for each streamtube as the solutes experience different physico-chemical properties of the aquifer material along each flowpath.

2.3 Numerical Evaluation of Breakthrough Curves

In order to evaluate the reaction function a simulation of the one-dimensional advective-reactive transport with respect to τ has to be conducted. The 'length' of the streamtube is given by the maximum travel time τ_{max} which may either be finite or infinite. The series of concentration profiles with respect to τ at time steps t_i ($i = 1, 2, \dots, n$) then approximate the reaction function Γ . As indicated in Fig. 1, any linear and nonlinear equilibrium reaction as well as kinetic processes such as intraparticle diffusion may be implemented in the 1D transport model.

The normalized breakthrough curve (BTC) of a reactive tracer at the control plane is given by

$$c(x, t) = \int_0^{\tau_{max}} g(\tau, x) \Gamma(\tau, t) d\tau \quad (1)$$

When applying a numerical model, the integral in eq. (1) is replaced by a finite sum yielding

$$c(x, t) = \sum_{i=1}^n g(\tau_i, x) \Gamma(\tau_i, t) \Delta\tau_i \quad (2)$$

$\Delta\tau_i$ is the discretisation of the one-dimensional streamtube model with respect to travel time τ and i is the time step index. Eq. 2 is used in the examples presented below.

Based upon these relationships the computer model SMART (Streamtube Model for Advective and Reactive Transport) has been developed. As indicated in Fig. 1, SMART accounts for hydraulic and physico-chemical aquifer heterogeneities as well as for equilibrium and kinetic reactive processes.

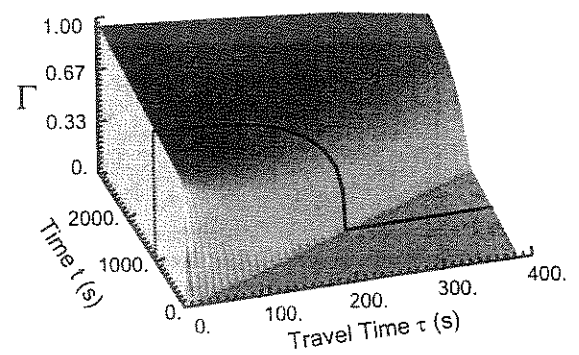


Figure 3: Reaction function Γ as a series of dimensionless concentration profiles over τ : example for $\tau_{max} \approx 400s$, solid line indicates profile for $t \approx 1000s$

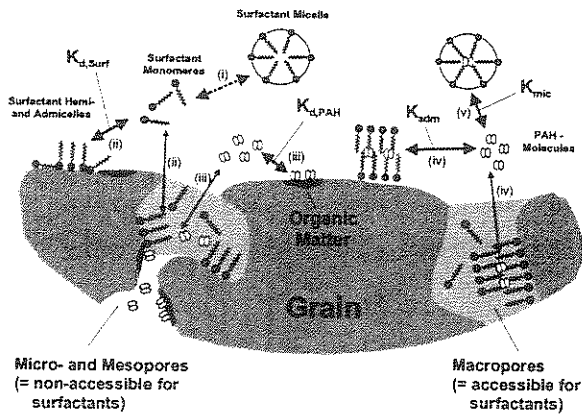


Figure 4: Conceptual model of processes relevant for coupled transport of PAH and surfactants at the laboratory scale: thick arrows indicate equilibrium reactions, thin arrows kinetic processes while the dashed arrow indicates an equilibrium relationship depending on critical micelle concentration (CMC)

2.4 Application to Coupled Transport of PAH and Surfactants at the Laboratory Scale

In order to apply SMART to simulate coupled transport of PAH and surfactants as solutes, a conceptual model of relevant processes has been developed by Finkel et al. [1997] (Fig. 4). Based on a close co-operation with laboratory investigations [Danzer and Grathwohl, 1997] during model development only those processes that could be identified within the lab experiments have been implemented in the model. Furthermore, process-oriented descriptions were used in order to guarantee that only measurable parameters are needed as model input. The conceptual model was verified and validated by column experiments. A total of 5 reactive processes have been identified as being relevant for the coupled transport of PAH and surfactant as solutes: (i) surfactant-micellization, (ii) surfactant sorption (formation of hemi- and admicelles) on exterior and intraparticle surfaces, (iii) PAH sorption on and into soil grains, (iv) PAH sorption on hemi- or into admicelles, (v) solution of PAH within micelles. The formation of micelles (i) occurs only if the surfactant concentration increases beyond a specific value, the so-called critical micelle concentration (CMC). Except the diffusion-limited processes of PAH and surfactant transport to intraparticle sorption sites all processes are assumed to be 'fast' and are described by equilibrium relationships. Heterogeneity of physico-chemical properties of the aquifer material is accounted for by introducing different grain size classes and lithological subcomponents.

3. FIELD SCALE SCENARIOS

In this section it will be shown qualitatively how surfactants may enhance the remediation of PAH-contaminated sites. To this end, a simple but typical scenario is considered (Fig. 5). Emphasis is put on the effect of large-scale hydraulic and physico-chemical heterogeneities on clean-up efficiency. In order to obtain a first insight into these relationships only equilibrium processes are considered. The role of intraparticle diffusion at field scale will be addressed within further research activities.

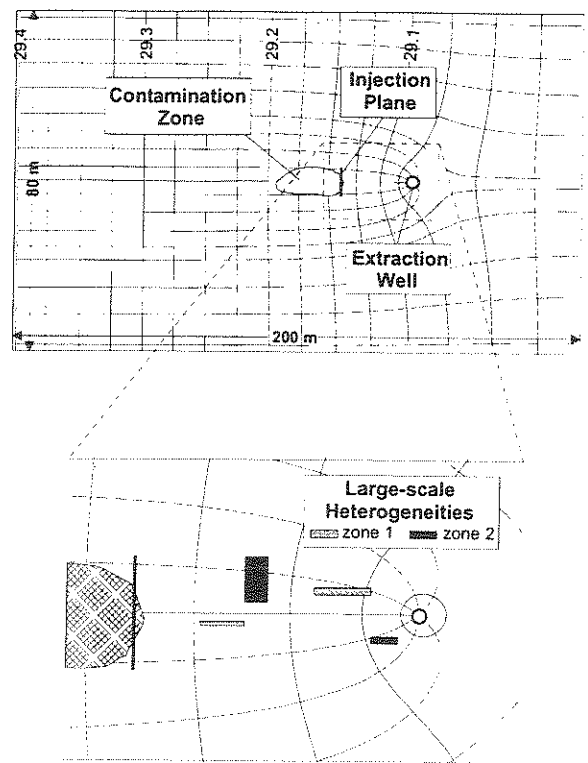


Figure 5: Simplified remediation scenario with large scale heterogeneities. Pathlines and isolines of hydraulic head for homogeneous model aquifer. Width of injection area is 10m, distance between extraction well and injection plane is 25m.

In the following, a confined porous aquifer of 20m thickness composed of Neckar river alluvial (NRA) with an averaged hydraulic conductivity $k_f = 10^{-3}m/s$ is considered. The gradient of the uniform flow field (inactive extraction well) is 0.2%. NRA is mainly composed of Triassic limestone, Jurassic limestone, sandstone and quartz with averaged mass fractions of 40%, 35%, 10% and 15%. Total and effective porosity are assumed with 40% and 20%, respectively. The pumping rate of the extraction well is for all simulations 2 L/s. Discrete zones are introduced to simulate the effect of large-scale heterogeneities. They are intended to take on different hydraulic and/or physico-chemical properties in comparison to the average of the surrounding aquifer. While zone 1 is intended to have a higher hydraulic conductivity and/or a lower sorption capacity, a lower hydraulic conductivity and/or higher sorption capacity may be assigned to zone 2. This inverse relationship between hydraulic conductivity and sorption distribution coefficients goes with other publications [e.g. Burr et al., 1994; Ptak, 1996]. The PAH phenanthrene (Phe) and the nonionic surfactant Terrasurf G50 (TG50) have been chosen as solutes. The behaviour of Phe and TG50 in NRA has been thoroughly investigated in the laboratory [Danzer and Grathwohl, 1997; Grathwohl and Kleinedam, 1995], so that all physico-chemical parameters used in the following simulations are available as measured quantities. The concentration of Phe at the injection plane was assumed to be constant at $c_0 = 200\mu g/l$ which is approximately the saturation concentration for Phe dissolving from the residual phase of a typical PAH mixture.

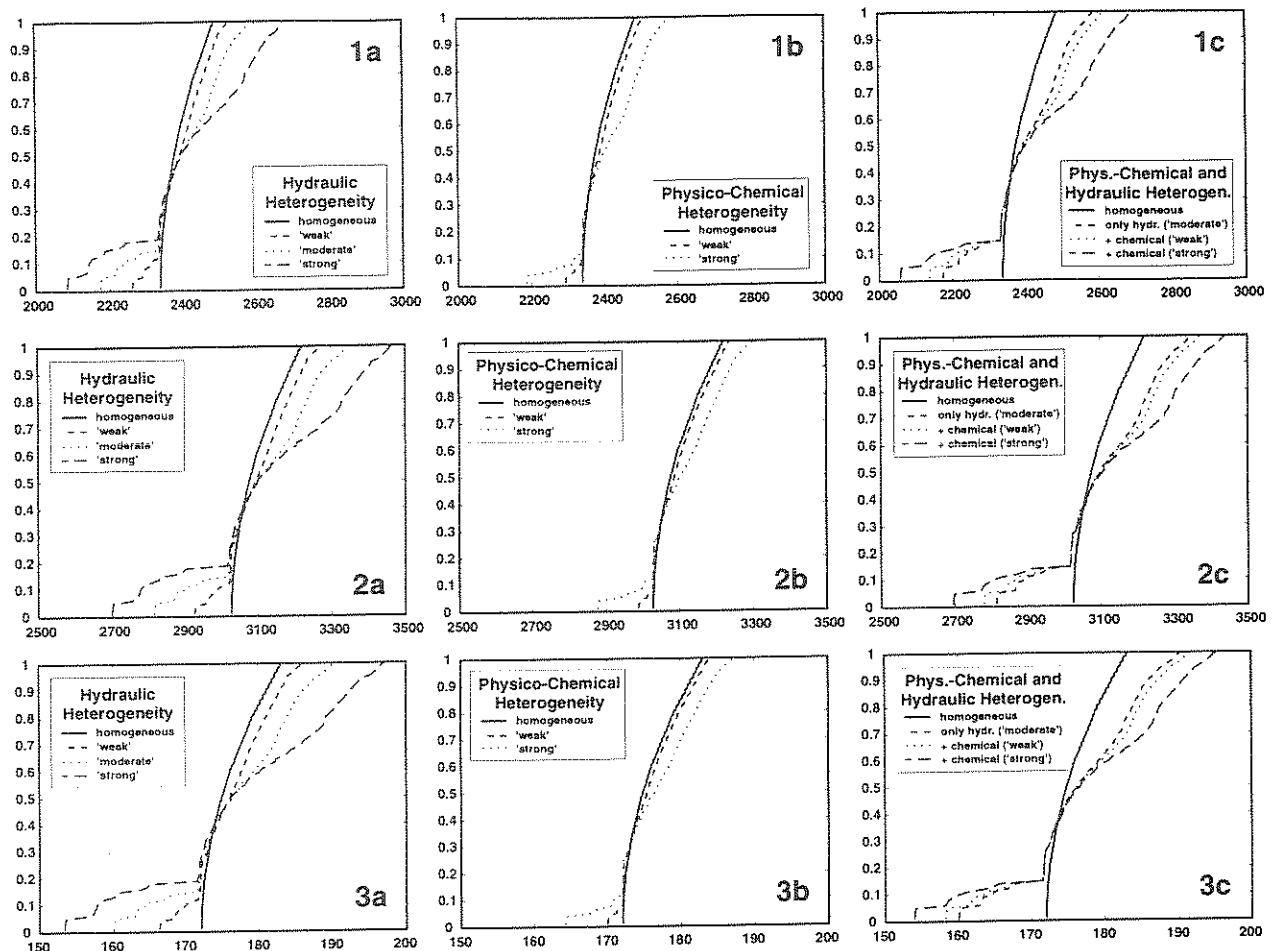


Figure 6: Simulation results: row 1 (Figures 1a – 1c) shows the breakthrough curves (BTC) of phenanthrene when no surfactant is present, row 2 shows phenanthrene BTC when Terrasurf G50 is present at a concentration equal to CMC, row 3 shows phenanthrene BTC when Terrasurf G50 concentration is 10 times CMC; column a (Figures 1a – 3a) shows the effect of hydraulic heterogeneity, column b shows the effect of physico-chemical heterogeneity, column c shows the effect of both hydraulic and physico-chemical heterogeneity; horizontal axis is time in days, vertical axis is relative phenanthrene concentration c/c_0

Hydraulic heterogeneity has been considered as 'weak' (conductivity of zone 1 is 1.2 times higher than the average, conductivity of zone 2 is 1.2 times lower than the average), 'moderate' (factor 1.5) and 'strong' (factor 2). Physico-chemical heterogeneity has been simulated by assigning lithological compositions to zones 1 and 2 which are different to the average. 'Weak' heterogeneity was simulated with relatively small deviations (35%–30%–15%–20% in zone 1 and 45%–40%–5%–10% in zone 2) while large deviations from average were introduced to model 'strong' heterogeneity (25%–20%–20%–35% in zone 1 and 65%–35%–0%–0% in zone 2). Note that here the term 'heterogeneity' only refers to large-scale heterogeneities and 'homogeneous' means evenly distributed heterogeneous aquifer material.

3.1 Pure Phenanthrene Transport

Pure phenanthrene transport is solely controlled by sorption onto solid phase. Sorption of Phe onto the lithological subcomponents being considered is assumed to follow sorption isotherms of the Freundlich type. The following isotherm parameters determined in batch experiments were used: for Triassic limestone the Freundlich coefficient K_{fr}

is 180 L/kg ($\mu\text{g}/\text{kg}; \mu\text{g}/\text{L}$) and the Freundlich exponent $1/n$ is 0.67, for Jurassic limestone $K_{fr} = 125 \text{ L/kg}$ and $1/n = 0.58$, for sandstone $K_{fr} = 30 \text{ L/kg}$ and $1/n = 0.66$ and for quartz $K_{fr} = 1 \text{ L/kg}$ and $1/n = 0.97$.

In Fig. 6.1 the BTCs of phenanthrene are presented for various degrees and types of heterogeneity. Figure 6.1a reveals that certain amounts of Phe particles are propagating through the low or high permeability zones while some particles are not affected at all by the discrete hydraulic heterogeneities. When only physico-chemical heterogeneities occur (Figure 6.1b) similar characteristics of the BTC can be observed. However, the impact of hydraulic heterogeneities appears to be superior. This can also be seen from the BTCs in Fig. 6.1c where the combined effect of physico-chemical and hydraulic heterogeneity is studied. Furthermore, it becomes apparent that the use of effective sorption parameters would not lead to a good representation of the aquifer properties with regard to predicting phenanthrene breakthrough.

3.2 Coupled Transport of PAH and Surfactant

As mentioned before, surfactants are able to either decrease ('adsolubilization') or enhance ('solubilization') PAH transport. Although TG50 – as a nonionic surfactant – is mainly

expected to enhance the transport of PAH, it is shown first to what extent TG50 may slow down the transport of Phe. This effect has become a point of interest as a useful alternative within protection systems such as permeable reactive walls [U.S. Environmental Protection Agency, 1995]. The maximum retarding effect on transport of organic contaminants such as PAH is achieved if the surfactant concentration in the liquid phase equals the critical micelle concentration (CMC) for the prevailing system. Then the concentration of sorbed surfactant monomers (ad- and hemimicelles) which constitute additional sorption sites for PAH reaches a maximum q_{max} . The CMC of TG50 in NRA in the presence of Phe was found to be 100 mg/L [Danzer and Grathwohl, 1997]. For the simulations it is assumed that the area between injection plane and extraction well has been entirely flushed with TG50 and sorbed surfactant concentration has reached q_{max} at any point of that area. In accordance with the laboratory results, q_{max} on Triassic limestone is 170 mg/kg, on Jurassic limestone 400 mg/kg, on sandstone 770 mg/kg and on quartz 40 mg/kg.

The retarding effect of TG50 at CMC on the phenanthrene transport is reflected by the BTCs in Fig. 6.2. In particular, Fig. 6.2a shows – in comparison to Fig. 6.1a – a slight increase in the hydraulic heterogeneity effects which might be explained by travel times, being generally longer in this case. The opposite effect occurs if only physico-chemical heterogeneities are assumed to exist (Fig. 6.2b). This results from opposing sorption affinities of Phe and TG50 to the lithological subcomponents sandstone and Triassic limestone. If both hydraulic and physico-chemical heterogeneities prevail these effects cancel each other out (Fig. 6.2c).

To show the solubilizing effect of TG50 on Phe transport a TG50 concentration in pore water of 1000 mg/L (10 times CMC) is assumed. Again it is supposed that the remediation area has been entirely flushed. This measure results in a dramatically decreased residence time of Phe (Fig. 6.3). The relative effect of hydraulic heterogeneities (Fig. 6.3a) and physico-chemical heterogeneities (Fig. 6.3b) is comparable to the previous scenario, while the absolute deviations from the homogeneous case are smaller.

Fig. 7 summarizes the results presented above. Without surfactants the expected travel time of Phe from the injection

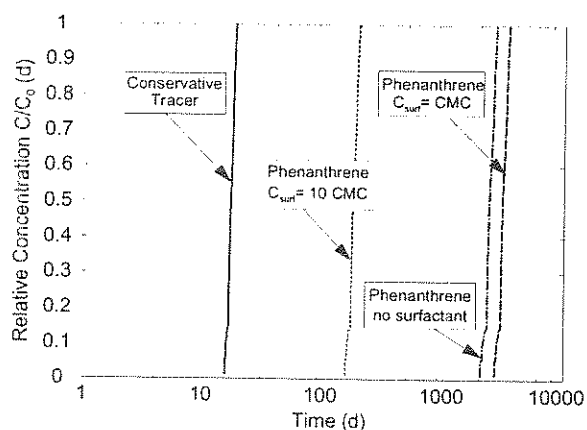


Figure 7: Simulated breakthrough curves of a conservative tracer and of phenanthrene in the presence of the surfactant Terrasurf G50.

plane to the extraction well is more than 100 times higher than for a conservative tracer. It is also shown that the solubilizing effect of TG50 on Phe transport may be of orders higher than its adsorbilizing effect. For higher TG50 concentrations than 10 times CMC used here an even higher solubilization may be achieved.

4. SUMMARY

A mathematical model has been developed to describe coupled reactive transport of PAH and surfactants as solutes in heterogeneous porous media. Both equilibrium and kinetic processes may be considered. The model has been verified and validated by means of one-dimensional studies [Finkel et al., 1997]. In this paper a simplified two-dimensional scenario is considered to show how in general the nonionic surfactant Terrasurf G50 influences the transport of phenanthrene as a solute. Both hydraulic and physico-chemical large-scale heterogeneities are simulated to assess their impact on phenanthrene and surfactant transport. All model parameters used here have been measured in laboratory experiments [Danzer and Grathwohl, 1997]. To study the potential retarding effect Terrasurf G50 is applied with a concentration equal to its critical micelle concentration (CMC) resulting in an additional retardation factor of 1.3. If a surfactant concentration well above CMC (10 times CMC) is applied, the residence time of phenanthrene between the contamination zone and the extraction well can be reduced by a factor of 14.

The Lagrangian approach and the modelling tool SMART have been proven to be applicable to 2D simulations of coupled reactive transport. Further research will also address 3D problems and sorption kinetics.

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