Accurate and efficient simulation of coupled water flow and nonlinear reactive transport in the saturated and vadose zone – application to surfactant enhanced and intrinsic bioremediation

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The reliable prediction of the fate of contaminants in the subsurface is a demanding task for modelers in the environmental sciences. We present a simulation tool that is capable of handling a variety of complex scenarios that are of interest for site remediation or natural attenuation. The modular model components include the Richards equation for (un-)saturated fluid flow which is discretized by locally mass conserving hybrid mixed finite elements. The transport equations contain (nonlinear) terms for equilibrium or kinetic sorption processes and biodegradation reactions. Microbial processes may be described by first order reactions leading to linear reaction networks or a multiplicative dual Monod model including electron donator, electron acceptor and biomass. Simulation of carrier facilitation or surfactant transport (including associated permeability changes and effects on surface tension of the fluid) are feasible as well. The systems of equations are treated with Newton’s method and adaptive techniques are applied to improve the efficiency of the implementation. We present an example of coupled surfactant migration and fluid flow. Current and future work includes the application to column experiments to investigate the potential of contaminated sites for natural attenuation and the extension of the model to geochemical multicomponent transport.

1. INTRODUCTION

For the investigation of the interaction of variably saturated flow and any contaminant migration in the subsurface it is essential to have a comprehensive flexible software tool at hand. By means of thorough simulations along with experimental studies relevant processes may be identified and understood, the effects of action variants estimated, or worst case scenarios predicted. We present such a software tool designed with a modular structure to facilitate the combination of existing and incorporation of new model components. It is beyond the scope of this paper to depict every process that has been integrated in the mathematical model with its defining equations in detail. We will restrict ourselves to a presentation of the general framework, designate the advanced mathematical solution strategies and exemplify two problems of interest for site remediation studies.

The tool named RICHY [1] currently solves (among others) the sets of partial differential equations corresponding to the following problem classes:
• Variably saturated flow

• Solute transport with (non-)linear equilibrium and kinetic sorption including carrier facilitation

• Biodegradation with three-component Monod-kinetics

• Surfactant transport interacting with fluid dynamics

• Multiphase flow

These modules may be combined to perform complex simulations and take the interactions of different processes into consideration. The appropriate description of the crucial factors in groundwater and soil pollution is essential. Consider e.g. the case of carrier facilitated transport, where strongly sorbing substances like polycyclic aromatic hydrocarbons become extremely mobile by sorbing on carrier substances like dissolved organic carbon and thus advection plays a major role in predicting travel times and the repartition of contaminant plumes. The coupling of unsaturated flow and carrier facilitated migration of phenanthrene in a layered soil profile has been demonstrated in [2]. RICHY is implemented in the language C, making use of OpenGL and Tcl/TK, and is thus portable to Unix, Linux and Windows-platforms.

2. SOME MODEL EQUATIONS

2.1. Fluid Flow

The description of the flow regime in the saturated and the vadose zone is based on the conservation of mass and Darcy's law. We establish the well known Richards equation for fluid flow in its pressure formulation:

$$\partial_t \Theta(p) + \nabla \cdot \bar{q} = 0 \quad \bar{q} = -\frac{k}{\mu} k_r(p) \nabla (p + \rho g z)$$

Here $t$ denotes the time, $\Theta$ the volumetric water content, $p$ is the pressure head, $\bar{q}$ the Darcy flux, $k$ is the intrinsic permeability of the porous medium, $\mu$ the viscosity, $k_r$ is the relative hydraulic conductivity, $\rho$ the density of the fluid, $g$ the acceleration due to gravity and $z$ is the elevation head.

This model is augmented with two coefficient functions: As indicated, the water content $\Theta$ is a function of the pressure head $p$ – the water retention curve – and the relative hydraulic conductivity $k_r$ depends as well on $p$ in a nonlinear form. For these functional relationships different parametrizations exist in the literature, and can be incorporated in the model. We added e.g. the van Genuchten - Mualem model, but also a form-free ansatz based on linear or quadratic spline interpolation that may be the result of an inverse modelling procedure for parameter identification, for which also efficient tools are integrated into RICHY [3].
2.2. Mass Transport – General Formulation

A general model for the transport of solutes dissolved in groundwater includes advection, dispersion, diffusion and general reaction terms (see e.g. [4]) reads

\[ \partial_t (\Theta c_i) - \nabla \cdot (D \nabla c_i - \bar{q} c_i) = \sum_{j=1}^{N_R} r_j. \]  

(2)

c_i denotes the solute concentration of species i, D is the diffusion-dispersion tensor, \( N_R \) is the total number of reaction terms and \( r_j \) the reaction rate of the \( j \)-th general reaction. These reaction terms may account for sorption phenomena, decay or other biogeochemical reactions and depend on other parameters or concentrations.

2.3. Biodegradation

Biodegradation models exist on different levels of complexity. Besides decay of 0th order with \( r_j = -\text{const} \) we may think of elementary, irreversible first-order decay, resulting in linear reaction networks \( X_1 \overset{k_1}{\rightarrow} X_2 \overset{k_1}{\rightarrow} \ldots \overset{k_{n-1}}{\rightarrow} X_n \) with terms

\[ r_j = r_j(c_{i-1}, c_i) = k_{i-1}c_{i-1} - k_i c_i \]  

(3)
in the equation for substance \( X_i \) (see e.g. [5] for analytical solutions). A more complex but also widely used model to quantify biodegradation rates in the subsurface is the so-called dual Monod-model [6]. It describes a system of three components, namely an organic substrate (the electron donator, index \( D \)), an electron acceptor (such as oxygen or nitrate, index \( A \)) and the biomass (index \( X \)) that is supposed to be immobile (see e.g. [7] for a systematic analysis of the model). Now we have for acceptor and donator rate expressions of the following form

\[ r = r(c_D, c_A, c_X) = -\mu_m \left( \frac{c_D}{K_D + c_D} \right) \left( \frac{c_A}{K_A + c_A + \frac{c_A}{K}} \right) c_X. \]  

(4)

Biomass benefits from the decay of the substances, thus we get a source term, along with a death rate \( d \) for the bacteria population:

\[ r = r(c_D, c_A, c_X) = Y \mu_m \left( 1 - \frac{c_X}{c_{X_{\text{max}}}} \right) \left( \frac{c_D}{K_D + c_D} \right) \left( \frac{c_A}{K_A + c_A + \frac{c_A}{K}} \right) c_X - dc_X. \]  

(5)

\( \mu_m \) is the maximum specific growth rate, \( K_D \) resp. \( K_A \) are the half-saturation constants, \( K_I \) is a Haldane inhibition factor, \( Y \) the yield coefficient and \( c_{X_{\text{max}}} \) the maximum microbial concentration. These biodegradation processes occur in both vadose and saturated zone, thus a coupling to the Richards equation is important. Current work deals with the application of this model to quantify the potential of contaminated sites for natural attenuation.

2.4. Surfactants: Mutual coupling of flow and transport

In the previous examples, the coupling of flow and transport was unidirectional in the sense that the flow considered as independent of the transport behaviour. In the case of
Surfactant transport however, transport affects fluid flow. Thus the coupling is a mutual one. In the last decade research on surfactant enhanced aquifer remediation (SEAR) advanced and mathematical formulations of the interaction of surface active agents and water flow can now be incorporated in numerical simulation tools. Surfactants alter the surface tension of the liquid phase, may mobilize entrapped NAPL or reduce the permeability of the porous medium by sorption. We extend the standard formulations of fluid flow and solute transport by taking two additional aspects into account:

According to findings of Smith and Gillham [8], [9] the surface active agent decreases the surface tension of the fluid with increasing concentrations and thus affects the capillary pressure of an unsaturated soil. Therefore a scaling factor is introduced in the pressure-saturation relation:

$$\Theta(p) \rightarrow \Theta\left(\frac{\sigma_0}{\sigma} p\right) =: \theta(p, c) \quad \frac{\sigma_0}{\sigma} = \frac{1}{1 - b \ln(c/a + 1)}$$

with empirical, surfactant dependent parameters $a$ and $b$.

The second effect is the reduction of the permeability due to the preferential sorption of the surfactant to the clay fraction of the soil, which increases due to the sorption. It is incorporated in the model according to [10]:

$$k \rightarrow k_{\text{eff}}(c) = k_{\text{coarse}}^{1-\nu} k_{\text{clay}}^{\nu} \quad \nu = \nu_{\text{clay}} + \frac{\rho_b}{\rho_s} \phi(c)$$

$$k_{\text{eff}}(c) k_r(p) =: K(p, c)$$

$k_{\text{eff}}$ represents the effective permeability, $k_{\text{coarse}}$ and $k_{\text{clay}}$ the saturated permeabilities of the coarse respectively the clay fraction of the soil, $\nu_{\text{clay}}$ is the volume fraction of the clay component and $\rho_b$ and $\rho_s$ are the densities of the bulk soil and the surfactant, respectively. As the surfactants have an influence on the flow regime, they do also affect the fate of a contaminant which is transported in the subsurface. An example for the simulation of surfactant migration in 2D is given in section 4.

3. DISCRETIZATION TECHNIQUES AND NUMERICAL METHODS

Advanced mathematical strategies come into operation in RICHY to guarantee the efficiency and accuracy of the calculations. The model equations are discretized by the fully implicit backward Euler method in time and by finite elements in space. The Richards equation and the coupled water/surfactant problem are discretized by mixed finite element methods to ensure the local conservation of mass and the continuity of the flux (also for heterogeneous media), a crucial quality for subsequent transport processes depending on that fluid flow. The standard conforming finite element method with mass lumping is used for the discretization of the other transport modules.

A damped version of Newton’s Method (Armijo’s rule) is used to solve the local and the global nonlinear equations that result from discretizing the partial differential equations. The global system of linear equations is solved by a multigrid method. Based on the equivalence of nonconforming and mixed finite elements the multigrid method is in this case built from grid transfer operators, derived for the Crouzeix-Raviart element [11]. The coarse grid matrices are defined by Galerkin approximation. The linear problem on
the base level of the grid hierarchy is solved by LU decomposition. On fine grid levels
smoothers like Gauss-Seidel or ILU are used.

Richy supports the usage of adaptive strategies to control the sizes of time steps and
grid spacing. The usage of such techniques ensures the efficient utilization of the available
performance of a computer, that otherwise would be restrictive for complex scenarios.
Using error indicators for the finite element discretization of the model equations, the grid
representing the underlying domain of the simulation may automatically be refined and
coarsened, corresponding to the form of the solution. Additional indicators for the error
of the time discretization allow for an adaptive time stepsize control. This automatic
adaptation of discretization parameters is currently implemented for (un-)saturated fluid
flow and will be applied also to the remaining model components. An example of adaptive
grid generation is given in [12].

4. NUMERICAL EXAMPLE

The introduced model is applied to visualize the effects of varying surface tension and
permeability in a two dimensional simulation with an artificial data set. All the results are
compared to the corresponding flow and transport scenario with constant surface tension
and without permeability reduction (labelled 'Reference' in Fig. 1 and Fig. 2).
The Richards equation is complemented by exponential parametrizations of the water
retention curve and the unsaturated hydraulic conductivity. We impose a stationary un-
saturated flow regime from the northern to the southern boundary of a square domain
by defining the flux and the corresponding initial pressure profile. Eastern and western
boundaries are impermeable (no flow boundaries). Thus when assuming no impact of the
surfactant transport on the water flow, the water content \( \theta = 0.295 \) (color-coded in Fig.
1 and Fig. 2 with green), the pressure and the flux remain constant throughout the entire
time interval.

For the transport of the surfactant, we included the effects of advection, diffusion, longi-
dudinal and transversal dispersion as well as linear equilibrium sorption. The substance
is injected at the western half of the northern boundary within the time interval \([0, 6]\),
after which no more surfactant enters the area. At the southern boundary a free outlet is
given (homogeneous Neumann condition). See the migration of the contaminant plume
at different time steps on the left hand side of Fig. 1 and Fig. 2.

In a first step we disregard pressure scaling and respect only the permeability reduction
through the sorptive capacity of the surfactant as proposed in model equation (7). As
the sorbed mass of surfactant per mass of soil \( \phi(c) \) is increasing, the effective hydraulic
conductivity \( K_{\text{eff}} \) will be dominated by the low conductivity of the clay fraction \( K_{\text{clay}} \) and
thus decrease. As we impose the same water flux at the boundaries as in our reference
case, this leads to a retarded water transport in the area of low permeability, thus an
increase in the water content (see right column of Fig. 1). As water flow is hindered
by the surfactant plume, the water content in front of the plume now decreases. The
permeability reduction induces the retardation of the surfactant migration, as can be
seen in the middle column of Fig. 1.

In a second simulation, we disregard the permeability reduction, but enable the surface
active agents to change the surface tension and thus affect the hydraulic pressure head
as described by model equation (6). Increasing surfactant concentration $c$ implies lower surface tensions and consequently higher pressure heads. As a consequence of the generated hydraulic gradient, water content decreases (right column of Fig. 2) with the solute front. If surface tension is assumed constant, increases in pressure head indicate increased water contents, i.e. a wetting front. But as demonstrated in a recent experimental study by [9] pressure heads may increase substantially while the water content decreases in the presence of surface active agents. This observation can be clearly reproduced by this two dimensional numerical simulation. Another remarkable effect is the change of the water flow in the eastern half of the domain. As water content decreases where the surfactant concentration is high, it increases in the eastern half, i.e. the flow is deviated towards the east. The constant water content in the reference case is $\theta = 0.295$. This explains the extended spreading of the surfactant plume (middle column of Fig. 2) in the transversal direction. Regarding the travel times, the surfactant migration is not retarded in this case.
A subsequent simulation of contaminant transport strongly depends on the water content and flux distributions that result from coupled water-surfactant transport. For an inert contaminant, i.e. neglecting sorption effects, the migration velocity is given by $\bar{q}/\Theta$. Not only the direction of the flux is altered but also the modification of water content will change this migration velocity. In addition the micellar pseudophase occurring at surfactant concentrations above a critical value acts as a solubilizer for organic solutes. Taking this solubilization into account, e.g. using the model of carrier facilitation (cp. [13]), is a next step for the model development.

5. CONCLUSIONS AND FUTURE WORK

We presented a simulation tool capable of treating complex flow and transport scenarios, in particular applications where steady state assumptions are not appropriate. This is the case e.g. for highly mobile components in the subsurface where variations of the fluid flow have an immediate impact on travel times and transport behaviour of
the contaminants. The application of the model allows us to study complex transport phenomena for a better understanding of the interactions of the underlying processes that have been identified in experimental studies. In current site remediation studies the tool is applied for estimating the potential of natural attenuation at several sites. Future work includes the extension of the model to geochemical reaction mechanisms based on thermodynamics including general kinetic reactions. This goal can only be achieved using flexible, accurate mathematical strategies that economize CPU and memory resources.

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REFERENCES