M^3 : a multiphase, multiconstituant and multiprocess code to model contaminated sites

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ABSTRACT

70% of the contaminated sites in France are with organic compounds (hydrocarbons, chlorinated solvents,…). Modeling such contamination can be difficult as it is governed by numerous and highly coupled mechanisms (multiphase flow, dissolution and volatilization of Non Aqueous Phase Liquids (NAPL), sorption and biodegradation). Whereas many numerical codes include some of these mechanisms, none of them, to our knowledge, allows the modeling of the full set of mechanisms. A new code, called M^3 for Multiphase, Multicomponent, Multiprocess, is then being developed to address this kind of modeling. The originality of the code stands both in the diversity of the mechanisms and in original formalisms such as non-local equilibrium dissolution of NAPL or biodegradation formalism dedicated to chlorinated solvents. After a short description of the numerical code, test cases will be presented to highlight the capacity of the code to model many situations that might be accoutered when dealing with contaminated sites (prediction of an accidental spill, temporal evolution of a source zone and its impact on aquifers, assessment of biodegradation…).

INTRODUCTION

A majority of contaminated site in France are with organic compounds such as hydrocarbons and chlorinated solvents. These contaminations implies a source zone (a non-aqueous phase liquid (NAPL)) a dissolved (and/or gaseous) contaminant plume migrating downstream (/ upward) and biodegradation processes. Therefore, the fate of these contaminants in the subsurface is driven by numerous and highly coupled mechanisms. Whereas many numerical codes include some of these mechanisms, none of them (to our knowledge) allows the modeling of the full set of mechanisms. Therefore, a new code called M^3 for Multiphase, Multicomponent, Multiprocess is being developed by a group of academic researchers (LHYGES, IMFT) and a consulting company (BURGEAP). In the following, are presented a description of the code functionalities that will be included and verification tests of already developed functionalities that highlight the code ability to model various contamination situations.

CODE DESIGN

M^3 is designed to model the fate of organic contaminant such as hydrocarbons and chlorinated solvents in the subsurface. As organic contamination can be in various phases (NAPL, dissolved in groundwater, volatilized in soil gas), multiphase flow is included in the code. A conservation equation for the three phases is then considered (here for the aqueous phase w):

$$\frac{\partial(\phi S_w \rho_w)}{\partial t} + \nabla\cdot(\rho_w \mathbf{u_w}) = I^w \qquad \mathbf{u_w} = \frac{\mathbf{K} kr_w}{\mu_w}\cdot(\nabla \mathbf{P_w} - \rho_w \mathbf{g})$$

where ϕ is the porosity, S_w and ρ_w are the saturation and the density, $\mathbf{u}_w$ is the velocity vector, I^w is a source/sink term, $\mathbf{K}$ is the permeability tensor, kr_w is the (saturation dependent) relative permeability μ_w is the viscosity, p_w the pressure and $\mathbf{g}$ the gravity vector. The contaminants are possibly under the three phases, a conservation equation is then required for every species (index i) in every phases (including the solid phase to follow the sorbed contaminants). For the aqueous phase, it reads:

$$\frac{\partial(\phi S_w \rho_w \omega_i^w)}{\partial t} + \nabla\cdot\left(\rho_w \omega_i^w \mathbf{u_w}\right) = \nabla\cdot\left(\phi S_w \rho_w \mathbf{D_i^w}\cdot\nabla\omega_i^w\right) + I_i^w$$

where ω_i^w is the mass fraction of the contaminant, $\mathbf{D_i^w}$ is the dispersion tensor and I_i^w is a source sink term that includes the mass transfer between phases (dissolution, volatilization, adsorption) and biodegradation processes. The originality of the code stands in the diversity of the mechanisms as well as in formalisms based on academic research work:

- the multicomponent diffusion in soil gas allows to describe the interaction of volatilized contaminants (Quintard et al, 2006) and therefore a fine prediction of their migration toward the surface ($\mathbf{D_i^w}$ depends on the gas composition (ω_1^w, ω_2^w,..., ω_n^w));
- the kinetic formalism for dissolution and volatilization processes (Coutelieris et al, 2006) allow to improve the prediction of the source zone long time depletion (dissolution/volatilization terms in I_i^w depend on the mass fraction of the contaminant in two phases) ;
- the kinetic formalism for adsorption is especially well-adapted to describe rebound effect that are observed after soil excavation (reference appropriée?) (the adsorption term in I_i^w depends on the mass fraction of the contaminant in two phases);
- the biodegradation package dedicated to contaminants families (petroleum hydrocarbons and chlorinated solvents) allow a fine prediction of contaminant fate when this mechanism is predominant (Nex et al, 2004).

The problem to solve is then a set of numerous partial differential equations (PDEs) that are highly coupled and nonlinear. The code is based on the mixed hybrid finite elements method and allows structured and unstructured grids. The numerical resolution follows the method of lines (Kees and Miller (2002), Fahs et al (2011)), which is well adapted to tackle scalable PDEs with non linearities. The solver is DLSODIS[1]. The Marquart-Levenberg method is used for non-linear systems and the linear solver is optimized for constant matrix and non evolutive structured matrix. The code benefits from an adaptative time step scheme. Finally, the code goes with an interface for functionalities and parameters settings and is related to preprocess and postprocess tools (Gmesh for geometry construction and mesh generation and Paraview for output visualization).

CODE VERIFICATION

M^3 has been validated against several analytical solutions and other numerical codes (not presented here). In what follows, we propose some tests aimed to highlight the code performances on problems of different nature.

Chlorinated solvent spill in an aquifer

The test focuses on the ability of the code to model hydrocarbons spill. Such model is useful to predict the impact of an accidental spill at the surface, i.e. to address the typical questions: how long before the contamination reach the water table? What concentration is expected in groundwater? In the test, the experiment of O'Carroll et al (2004) was simulated; it consists in a NAPL infiltration (tetrachloroethylene (PCE)) in a water saturated sandbox with heterogeneity zones. The comparison between the experiment, the simulation conducted by O'Caroll et al (2004) and the M^3 result shows good agreement (Figure 1). Besides, this test allows to check that the code correctly reproduce the infiltration front driven by capillary and gravity effects.

[1] Solver DLSODIS was developed by Alan C. Hindmarsh et Sheila Balsdon (Lawrence Livermore National Laboratory, version nov. 2003)

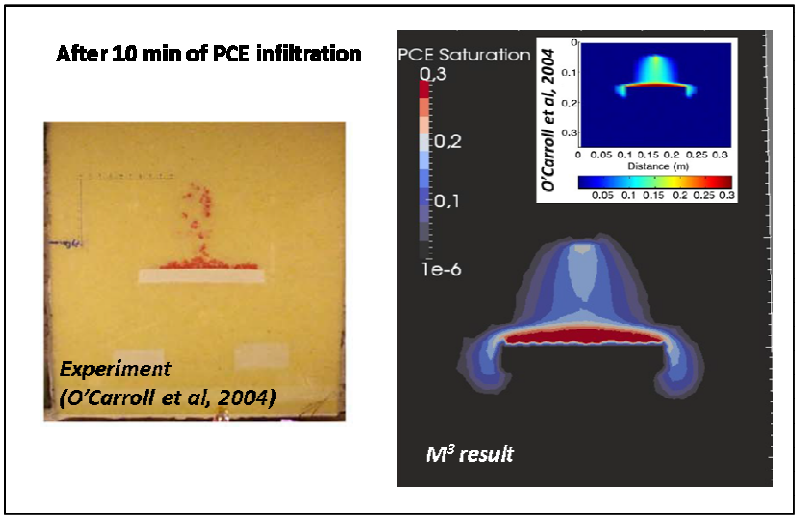

Figure 1. Verification test on NAPL infiltration in a sandbox

Source zone depletion in a saturated medium

The test focuses on the ability of the code to reproduce the dissolution of an immobile NAPL (i.e. the source zone) composed of chlorinated solvents in groundwater. Besides verification purpose, the test is conducted to highlight the importance of the non-local equilibrium formalism to reproduce the tailing effect that characterizes the source zones depletion at low saturation. In the test, an immobile NAPL (tetrachloroethylene (PCE) and trichloroethene (TCE)) is placed in a saturated homogeneous porous medium. Water flow is driven by constant pressure boundary conditions at the two ends of the domain. Only dissolution and convection-dispersion in aqueous phase are modeled (No adsorption and biodegradation). The test is also conducted with Modflow-Surfact for comparison purpose. The main differences between the two codes stand in the resolution method (finite elements *versus* finite differences), the dissolution formalism (non-local *versus* local equilibrium) and the influence of NAPL on water flow (not considered in Modflow-Surfact). Despite these differences, the results show good agreement in source zone evolution and dissolved plume profile (Figure 2).

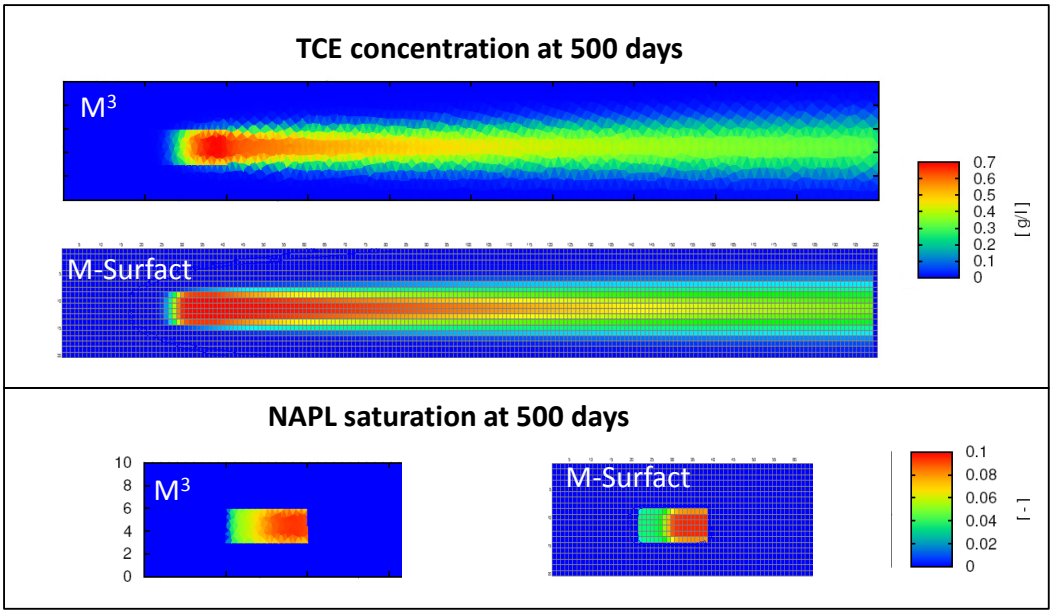

Figure 2. Verification test of NAPL depletion and dissolved contaminant transport in a porous media

Biodegradation of chlorinated solvents in groundwater

This test is similar to the previous one with the addition of the biodegradation. The chloroethenes biodegradation is characterized by various reactions depending on the redox conditions (see Nex et al (2004) for details). M^3 and Modflow-Surfact are again compared. Whereas the biodegradation process in M^3 follows the complex formalism of Nex et al (type of reactions according to redox conditions, Monod kinetics, competition between electron acceptors,…), the test with Modflow-Surfact is conducted with sequential reactions (first order kinetics) with homogeneous reaction constants. The comparison highlights the difficulties to reproduce biodegradation of chloroethenes with a simple formalism such as the one used in Modflow-Surfact (Figure 3).

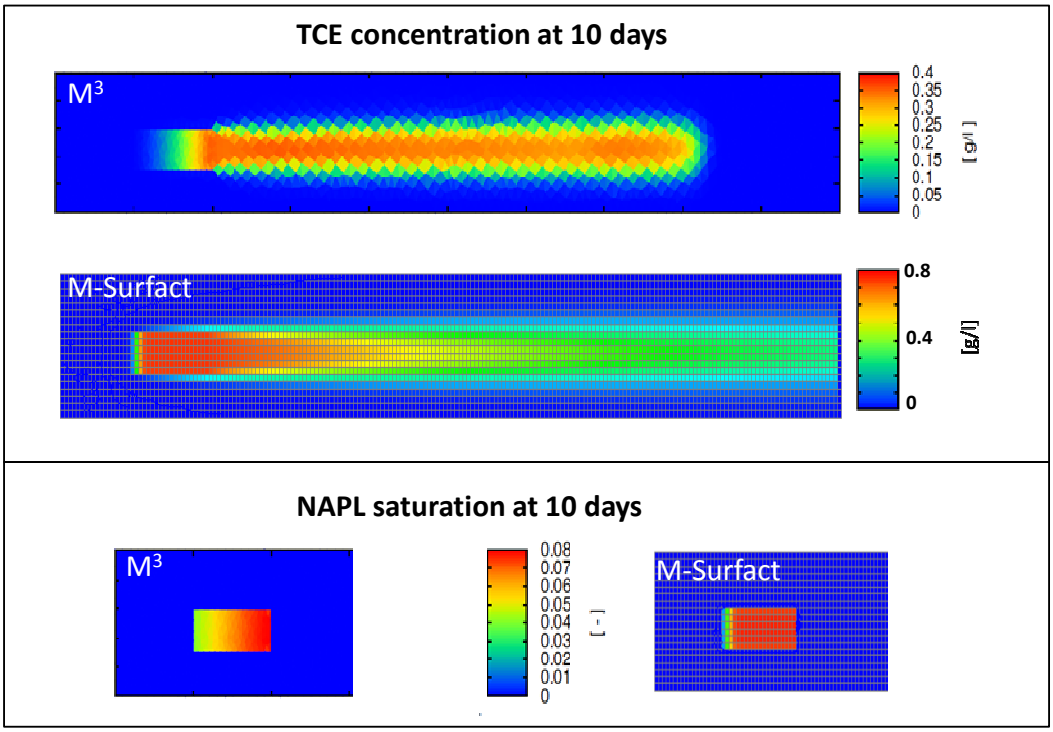

Figure 3. Verification test of chloroethenes biodegradation in groundwater

CONCLUSION

The M^3 code is dedicated to the modeling of organic contaminant fate in subsurface by integrating all the implied mechanisms (multiphase flow, mass transport in phases, dissolution, volatilization, adsorption, biodegradation). The code is based on original formalisms for a better prediction of various contamination situations. The presented test highlights the performance of the code to model some contamination situations with fine precision.

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