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FINITE ELEMENT METHODS FOR SOLVING CONTAMINANT TRANSPORT PROBLEMS

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Abstract. The aim of this work is the comparison between two finite element approaches for solving multispecies contaminant transport problems together with sorption and biodegradation processes which can take place inside a porous matrix aquifer characterizing a stage of subsurface contamination by organic contaminants. Mathematically the problem is described by a nonlinear advection-diffusion-reaction partial differential system coupled by reaction terms which are associated to the kinetics that govern biodegradation processes.

Computational aspects obtained via numerical simulations of a standard fully coupled technique and an operator splitting approach are analyzed. This second methodology deals with convective-diffusive and reactive terms in a sequential way, producing an efficient and natural alternative to numerical solve different types of biodegradation kinetics and sorption conditions. For both methodologies a predictor-multi corrector algorithm with Newton-Raphson and stabilized finite element methods are used in time and spatial discretizations, respectively, to approximate the nonlinear transport equations.

Efficiency and accuracy to the proposal methodologies are analyzed via three typical contamination scenarios where nonlinear biodegradation processes, equilibrium and non-equilibrium sorption conditions are carried out. This study allow us to choose the most convenient approach for each case. The operator splitting procedure is very attractive for parallel computation, large multidimensional problems with multiple species, treating in a novel way different types of biodegradation kinetics and sorption conditions. On the other hand, fully coupled techniques are mathematically considered more rigorous procedures, and they have been generally employed to solve nonlinear reactive transport problems.

1 INTRODUCTION

Groundwater contamination by organic compounds is a problem, that can be solved or reduced by remediation technologies. Among efficient and known strategies are those that utilizes *in situ* biodegradation (biological) processes (Gallo and Manzini , 2001). Furthermore, another important and usually regardless phenomenon, which occurs in the aquifer porous matrix, is the contaminant sorption (van Genuchten and Wagenet , 1989) which can interfere in the contaminant plume propagation velocity. Therefore understanding the influence of these physical and biological processes on the bioremediation effectiveness of contamination scenarios can be very useful.

Contaminant transport problems under biodegradation kinetics and sorption in equilibrium and non-equilibrium conditions had extensively been studied in the last years. Many or most of these works have considered these processes separately (Hokr and Maryska , 2002; Kacur et al. , 2005; Remesikova , 2004; Serrano , 2001; Toride et al. , 1993; van Kooten , 1996) or have taken only into account nonlinear sorption conditions combined with linear biodegradation kinetics (Frolkovic and Kacur , 2006; Kanney et al. , 2003a,b). However important environmental problems hence require a simultaneous analysis of the physical and biological processes, which can interfere in the fate and transport of the pollutant. Thus we have being studied (Couto , 2006; Couto and Malta , 2008) a mathematical model that governs a two species transport problem, with mass transfer between solid and aqueous phases, and nonlinear biodegradation and sorption reactions, in a one-dimensional saturated porous medium. The system coupling is done via the reaction terms. A fully coupled (FC) technique and an operator splitting (OS) approach were proposed in order to numerically solve the mentioned contaminant problem. These methodologies provided physically acceptable solutions, taking into account a rigorous evaluation of the nonlinear terms and a special treatment of the predominately convective character of the transport equation (biodegradation is a predominant convective phenomenon) (Wheeler and Dawson , 1987). For both methodologies the SUPG (Streamline Upwind Petrov-Galerkin) stabilized finite element method (Brooks and Hughes , 1982) in space and a predictor-multi corrector algorithm in time are used to approximate the predominant convective transport equations. In addition, the nonlinearities associated with the sorption conditions, biodegradation processes and the system uncoupling (reaction terms) are performed via a Newton-type method by the FC approach. Therefore, it can be viewed as a fully coupled numerical model in the sense that the differential operators describing the governing equations are approximate as a complete system. On the other hand, the OS methodology solves the ordinary differential equations, corresponding to biodegradation kinetics and sorption in non-equilibrium mode using a fourth-order Runge-Kutta method (Odencrantz et al. , 1993).

From the mathematical point of view FC numerical methodologies are considered rigorous procedures, and they have been generally employed to solve nonlinear reactive transport problems (Farthing et al. , 2006; Gallo and Manzini , 2001; Herzer and Kinzelbach , 1989; Kanney et al. , 2003b; Karapanagioti et al. , 2001). In fact, for each time step, the temporal FC approximation is applied to a semi-discrete stabilized finite element (SUPG) equation which comes from the original problem and has solid mathematical bases. In this way, connections among the operator in each equation are maintained and both nonlinearities and species coupled problems are solved via an iterative algorithm associated to the usual Newton method. On contrary, the OS methodology decouples the differential equations of the original model in two parts, namely: one related to the transport and the other to the reaction. Therefore, each part is approximated by the most suitable numerical technique associated with its operator. The OS applicability mainly depends on two factors: the reduction of possible errors caused by the decomposition of the coupled set of equations and the convergence to the exact solution due to time step size reduction.

The objective of the present paper is to study numerical aspects related to FC and OS numerical schemes performance (robustness, accuracy and CPU time execution, for example) when applied to three typical contaminant scenarios. For doing this, the paper is organized as follows: we start with a general two species nonlinear reactive transport model considering biodegradation reactions and equilibrium and non-equilibrium sorption conditions; next, we define the fully coupled numerical methodology and the operator splitting procedure that will be analyzed under some computation points of view. Finally the paper ends with a summary of the main conclusions.

2 THE NONLINEAR CONTAMINANT TRANSPORT MODEL

The complete nonlinear coupled mathematical model describing a two species transport problem, with mass transfer between solid and aqueous phases, and biodegradation reactions, in a one-dimensional saturated porous medium, is given by

$$\frac{\partial F(C_1)}{\partial t} + V\frac{\partial C_1}{\partial x} - D\frac{\partial^2 C_1}{\partial x^2} + \frac{\partial S_1}{\partial t} + R_1(C_1, C_2, b_1) = 0, \tag{1}$$

$$\frac{\partial S_1}{\partial t} = K(\Psi(C_1) - S_1), \tag{2}$$

$$\frac{\partial C_2}{\partial t} + V\frac{\partial C_2}{\partial x} - D\frac{\partial^2 C_2}{\partial x^2} + R_2(C_1, C_2, b_1) = 0, \tag{3}$$

$$\frac{\partial b_1}{\partial t} = R_3(C_1, C_2, b_1). \tag{4}$$

for all $x \in (0, L)$ and $t > 0$, where C_1 and S_1 are the electron donor (contaminant) aqueous and solid phase concentrations, C_2 is the electron acceptor (oxygen) aqueous concentration, and b_1 is the bacterial biomass concentration. Function

$$F(C_1) = C_1 + \Phi(C_1) \tag{5}$$

with $\Phi(\cdot)$ and $\Psi(\cdot)$ defining the equilibrium and non-equilibrium sorption isotherms, respectively, commonly represented using either Freundlich or Langmuir isotherms (Farthing et al. , 2006; Frolkovic and Kacur , 2006; Kanney et al. , 2003a,b; Remesikova , 2004). Following Odencrantz et al. (1993) we assumed that sorption occurs only to the electron donor (the contaminant) and the sorption conditions are modeled by Freundlich isotherms, that is, $\Phi(\cdot)$ and $\Psi(\cdot)$ are given by

$$\Psi(C_1) \text{ and/or } \Phi(C_1) = K_0(C_1)^p, \tag{6}$$

where $K_0 > 0$ is the sorption capacity coefficient and $p > 0$ the measure of the sorption intensity. In equations (1) and (3) the velocity (V) and the diffusion coefficient (D) are positive constants. In order to avoid the diffusion coefficient influence on the reactive interaction analysis we take the same diffusion coefficient for both equations (Farthing et al. , 2006; Kacur et al. , 2005; Kanney et al. , 2003a; Odencrantz et al. , 1993). However, different values may be considered Merz (2005).Finally, $R_j(\cdot, \cdot, \cdot)$, $j = 1,\ 2,\ 3$ are biodegradation kinetic expressions (minimum-rate Monod, as defined in subsection 5.2) and K is a first-order mass transfer coefficient for mass transfer between the aqueous phase and the slowly sorbing solid phase (Kanney et al. , 2003a).

In addition, it is necessary to equip the coupled nonlinear diffusive-convective-reactive transport system (1)-(4) with appropriate boundary and initial conditions. Thus, we impose usual Dirichlet and Neumann boundary conditions for C_1 and C_2, that is:

$$C_1(0,t) = \bar{C}_1, \quad \frac{\partial C_1(L,t)}{\partial x} = 0, \tag{7}$$

$$C_2(0,t) = \bar{C}_2, \quad \frac{\partial C_2(L,t)}{\partial x} = 0. \tag{8}$$

The initial conditions are:

$$C_1(x,0) = C_1^0, \quad S_1(x,0) = \Psi(C_1^0), \tag{9}$$

$$C_2(x,0) = C_2^0, \quad b_1(x,0) = b_1^0. \tag{10}$$

All constant values in Eqs. (7)-(10) will be taken from the literature (Celia et al. , 1989; Kacur et al. , 2005; Odencrantz et al. , 1993; Remesikova , 2004, 2007) and use in the numerical simulations discussed here.

3 THE FULLY COUPLED NUMERICAL METHODOLOGY

The FC numerical methodology numerically handles with system (1)-(4) in the sense that the differential operators describing the governing equations are approximate as a complete system. Therefore, let $0 = t^0 < t^1 < t^2 < ... < t^N = T$ be a uniform temporal discretization of the interval $I = (0,T)$, $T > 0$ the final time, $I_n \equiv (t^n, t^{n+1})$, $n = 0,\ldots,N-1$ and the time step $\Delta t = t^{n+1} - t^n$ with $N = T/\Delta t$, considering the Crank-Nicolson second order finite-difference method approximating the time derivatives in Eqs.(1) and (3). Therefore, the complete (spatial and time) approximation is obtained applying the SUPG finite element method (Brooks and Hughes , 1982; Coutinho et al. , 2004; Johnson et al. , 1984) in the spatial discretization of variables C_1 and C_2. In this case, the domain Ω is partitioning in N_e elements with $h = \Delta x = L/N_e$ size. Each element Ω_e is such that $\bar{\Omega} = \bigcup_{e=1}^{N_e} \bar{\Omega}_e$ with $\bigcap_{e=1}^{N_e} \Omega_e = \emptyset$. Therefore, the fully discrete equations are written by:

(i) Given $C_1^{n-1,h}$, $C_2^{n,h}$, $S_1^{n,h}$ and $b_1^{n,h}$, find, $\forall n = 1,...,N$, $C_1^{n,h} \in V_1^h$ such that

$$\int_\Omega \mathcal{R}_1(C_1^{n,h}) w^h dx + \sum_{e=1}^{N_e} \int_{\Omega_e} \mathcal{R}_1(C_1^{n,h}) \tau V \frac{\partial w^h}{\partial x} dx = 0 \ \ \forall w^h \in W^h, \tag{11}$$

(ii) Given $C_2^{n-1,h}$, $C_1^{n,h}$ and $b_1^{n,h}$, find, $\forall n = 1,...,N$, $C_2^{n,h} \in V_2^h$ such that

$$\int_\Omega \mathcal{R}_2(C_2^{n,h}) w^h dx + \sum_{e=1}^{N_e} \int_{\Omega_e} \mathcal{R}_2(C_2^{n,h}) \tau V \frac{\partial w^h}{\partial x} dx = 0 \ \ \forall w^h \in W^h. \tag{12}$$

Expressions $\mathcal{R}_j(C_j^{n,h})$, $j = 1,2$ are the time semi-discrete residual terms of the transport equations obtained after applying the Crank-Nicolson method. The upwind parameter τ is defined by $\tau = h\xi(Pe)/2|V|$ (Brooks and Hughes , 1982), where $\xi(Pe) = coth(Pe) - (1/Pe)$ with $Pe = |V|h/2D$ the grid Péclet number (dimensionless), which evaluates the relationship between the convective and dispersive terms. V_i^h and W^h are the finite counterparts of spaces $V_i =$

$\{c_i(x) \in H^1(\Omega); c_i(0) = \bar{C}_i\}$, $i = 1, 2$ and $W = \{w(x) \in H^1(\Omega); w(0) = 0\}$. According to the finite element method, the approximate function $C_i^{n,h}$ is defined as: $C_i^{n,h}(x) = \sum_{l=1}^{nnode} C_{i,l}^n \varphi_l(x)$, $\forall x \in \Omega$, where $nnode$ is the number of nodes, $C_{i,l}^n$ the nodal value of $C_i^{n,h}$, with $\varphi_l(x)$ the shape functions. Hereafter, to simplify the notation, the subscript h, associated with the finite element discretization, is left behind and we also replace $C_i^{n,h}$ by c_i^n, $S_1^{n,h}$ by s_1^n and $b_1^{n,h}$ by b_1^n.

Therefore, an iterative algorithm based on Newton and Picard methods are exhibited to treat the nonlinearities and the coupling inserted by sorption and biodegradation expressions. The nonlinear functions $F(\cdot)$, $\Psi(\cdot)$ and $R_j(\cdot,\cdot,\cdot)$, $j = 1, 2, 3$, in the iteration step k, are approximated by tangent curves at the $c_i^{n,k-1}$, $i = 1, 2$ points, namely:

$$F(c_i^{n,k}) \approx F(c_i^{n,k-1}) + \frac{dF(c_i^{n,k-1})}{dC_i}(c_i^{n,k} - c_i^{n,k-1}), \tag{13}$$

$$\Psi(c_i^{n,k}) \approx \Psi(c_i^{n,k-1}) + \frac{d\Psi(c_i^{n,k-1})}{dC_i}(c_i^{n,k} - c_i^{n,k-1}), \tag{14}$$

$$\begin{aligned} R_j(c_1^{n,k}, c_2^{n,k}, b_1^{n,k},) &\approx R_j(c_1^{n,k-1}, c_2^{n,k-1}, b_1^{n,k-1}) \\ &+ \frac{dR_j(c_1^{n,k-1}, c_2^{n,k-1}, b_1^{n,k-1})}{dC_j}(c_1^{n,k} - c_1^{n,k-1}), \end{aligned} \tag{15}$$

Substituting the above expressions, Eqs. (13)-(15), into the residual terms $\mathcal{R}_j(\cdot)$, $j = 1, 2$, we arrive at linearized fully discrete transport problems. Finally, a Newton-type iterative scheme is employed to solve the complete discretized system taking into account solid phase and bacterial growth approximations. Hence, the solution in each time t^{n+1} is found when the solutions into two consecutive iterations are sufficiently near, that is, $||x^k - x^{k-1}|| = máx_{p=1}^{nnode} ||x_p^k - x_p^{k-1}|| < tol$, where tol is a previously established tolerance.

The introduced FC methodology numerical performance was verified on some computational simulations exhibited in Couto (2006). The effects of sorption and biodegradation processes under the plume contaminant transport were examined, reinforcing that nonlinear sorption should be coupled with convective transport models to accurately predict bioremediation alternatives, such as natural attenuation.

4 THE OPERATOR SPLITTING PROCEDURE

Comparing with other schemes in the literature (Frolkovic and Kacur , 2006; Kacur et al. , 2005; Kanney et al. , 2003a; Karapanagioti et al. , 2001; Odencrantz et al. , 1993), the main contribution of the following OS technique focuses on the introduction of both nonlinear equilibrium and non-equilibrium sorption combined with biodegradation kinetics. A brief description is explained below, more details can be found in Couto and Malta (2008). For n fixed, $n = 0, \ldots, N-1$, we firstly solve the following nonlinear uncoupled transport subsystem at t^{n+1}

$$\frac{\partial F(C_1)}{\partial t} + V\frac{\partial C_1}{\partial x} - D\frac{\partial^2 C_1}{\partial x^2} = 0, \tag{16}$$

$$\frac{\partial C_2}{\partial t} + V\frac{\partial C_2}{\partial x} - D\frac{\partial^2 C_2}{\partial x^2} = 0, \tag{17}$$

where the electron donor equation (Eq. (16)) is associated with nonlinear sorption in equilibrium mode via the $F(\cdot)$ function (see Eq. (5)). Next, in the same time level, we locally calculate the nonlinear reaction equations, that is

$$\frac{\partial C_1}{\partial t} + \frac{\partial F(C_1)^{-1}}{\partial C_1}\left(\frac{\partial S_1}{\partial t} + R_1(C_1, C_2, b_1)\right) = 0, \tag{18}$$

$$\frac{\partial S_1}{\partial t} = K(\Psi(C_1) - S_1), \tag{19}$$

$$\frac{\partial C_2}{\partial t} + R_2(C_1, C_2, b_1) = 0, \tag{20}$$

$$\frac{\partial b_1}{\partial t} = R_3(C_1, C_2, b_1), \tag{21}$$

considering the solution of system (16)-(17) as the initial conditions to the variables C_1 and C_2. Then, the evaluation of Eqs. (18)-(21) is the approximate solution for the mathematical model (1)-(4) at time $t^{n+1} \in I$. This cycle is repeated N time steps until the final time of interest is reached. The nonlinearities in Eqs. (18)-(21) are related to sorption in both conditions as well as the biodegradation processes. To numerically solve the diffusive-convective transport problem (16)-(17) (first stage) we use a semi-discrete stabilized finite element approach (the SUPG method), following the same strategy employed by the FC approach defined in the last section.

The nonlinear Eq. (16) was taken as a model problem to illustrate the adopted OS scheme. However, Eq. (17) can be analogously solved. According to the introduced notation the spatial discretization of Eq. (16) leads to an ordinary differential system, which is written in the matrix form:

$$\mathbf{M}(\mathbf{C_1})\dot{\mathbf{C}}_\mathbf{1} + \mathbf{K}\mathbf{C_1} = \mathbf{0} \tag{22}$$

where for all $i, j = 1, ..., nnode$ we have

$$[\mathbf{M}(\mathbf{C_1})]_{ij} = \int_\Omega \frac{\partial F\left(\sum_{j=1}^{nnode} c_{1,j}(t)\varphi_j(x)\right)}{\partial C_1}\varphi_j(x)\left(\varphi_i(x) + \tau V\frac{\partial \varphi_i(x)}{\partial x}\right)dx, \tag{23}$$

$$[\dot{\mathbf{C}}_\mathbf{1}]_j = \frac{\partial c_{1,j}(t)}{\partial t}, \tag{24}$$

$$\begin{aligned}[\mathbf{K}]_{ij} = &\int_\Omega V\frac{\partial \varphi_j(x)}{\partial x}\left(\varphi_i(x) + \tau V\frac{\partial \varphi_i(x)}{\partial x}\right)dx + \\ &\int_\Omega D\frac{\partial \varphi_j(x)}{\partial x}\frac{\partial \varphi_i(x)}{\partial x}dx - \sum_{e=1}^{Ne}\left(\int_{\Omega_e} D\frac{\partial^2 \varphi_j(x)}{\partial x^2}\tau V\frac{\partial \varphi_i(x)}{\partial x}dx\right),\end{aligned} \tag{25}$$

$$[\mathbf{C_1}]_j = c_{1,j}(t). \tag{26}$$

Hence, the fully discrete system associated to Eq. (16) reads

$$\mathbf{M}(\tilde{\mathbf{C}}_{\mathbf{1},n+1} + 0.5\Delta t\dot{\mathbf{C}}_{\mathbf{1},n+1})\dot{\mathbf{C}}_{\mathbf{1},n+1} + \mathbf{K}\tilde{\mathbf{C}}_{\mathbf{1},n+1} + 0.5\Delta t\mathbf{K}\dot{\mathbf{C}}_{\mathbf{1},n+1} = \mathbf{0}, \tag{27}$$

where $\tilde{\mathbf{C}}_{\mathbf{1},n+1} = \mathbf{C}_{\mathbf{1},n} + 0.5\Delta t\dot{\mathbf{C}}_{\mathbf{1},n}$. To solve the nonlinear problem (27) we apply the Newton-Raphson method for each time step as explained in the Algorithm 1 below, where we denote:

$$\mathbf{F}(\dot{\mathbf{C}}_{\mathbf{1},n+1}) = (f_1(\dot{\mathbf{C}}_{\mathbf{1},n+1}), f_2(\dot{\mathbf{C}}_{\mathbf{1},n+1}), ..., f_{nnode}(\dot{\mathbf{C}}_{\mathbf{1},n+1})), \tag{28}$$

with

$$f_i(\dot{\mathbf{C}}_{n+1}) = \sum_j [\mathbf{M}(\tilde{\mathbf{C}}_{n+1} + \Delta t\alpha\dot{\mathbf{C}}_{n+1})]_{ij}(\dot{\mathbf{C}}_{n+1})_j + [\mathbf{K}]_{ij}(\tilde{\mathbf{C}}_{n+1})_j + \Delta t\alpha[\mathbf{K}]_{ij}(\dot{\mathbf{C}}_{n+1})_j, \tag{29}$$

and

$$\mathbf{F}'(\dot{\mathbf{C}}^k_{\mathbf{1},n+1}) = \left[\frac{\partial f_i(\dot{\mathbf{C}}^k_{\mathbf{1},n+1})}{\partial(\dot{\mathbf{C}}_{\mathbf{1},n+1})_j}\right], \tag{30}$$

for all $i, j = 1, ..., nnode$. The linearization (delay) is included in the iterative part of Algorithm 1, that is, in the calculation of the residue $\mathbf{R}^k$ and the Jacobian $\mathbf{J}^k$.

Algorithm 1

```
Require: $\dot{\mathbf{C}}^0_{\mathbf{1},n+1} = \mathbf{0}$, $\mathbf{C}^0_{\mathbf{1},n+1} = \tilde{\mathbf{C}}_{\mathbf{1},n+1} = \mathbf{C}_{\mathbf{1},n} + 0.5\Delta t\dot{\mathbf{C}}_{\mathbf{1},n}$, $tol$, $k_{max}$, $\mathbf{F}$ and $\mathbf{F}'$,
Ensure: $\dot{\mathbf{C}}_{\mathbf{1},n+1}$ and $\mathbf{C}_{\mathbf{1},n+1}$
for $k = 0, 1, ..., k_{max}$ do
    $\mathbf{R}^k = -\mathbf{F}(\dot{\mathbf{C}}^k_{\mathbf{1},n+1})$
    $\mathbf{J}^k = \mathbf{F}'(\dot{\mathbf{C}}^k_{\mathbf{1},n+1})$
    solve $\mathbf{J}^k\mathbf{\Delta}\dot{\mathbf{C}}^{k+1}_{\mathbf{1},n+1} = \mathbf{R}^k$ and find $\mathbf{\Delta}\dot{\mathbf{C}}^{k+1}_{\mathbf{1},n+1}$
    $\dot{\mathbf{C}}^{k+1}_{\mathbf{1},n+1} = \dot{\mathbf{C}}^k_{\mathbf{1},n+1} + \mathbf{\Delta}\dot{\mathbf{C}}^{k+1}_{\mathbf{1},n+1}$
    $\mathbf{C}^{k+1}_{\mathbf{1},n+1} = \mathbf{C}^0_{\mathbf{1},n+1} + \alpha\Delta t\dot{\mathbf{C}}^{k+1}_{\mathbf{1},n+1}$
    if $\left(||\mathbf{\Delta}\dot{\mathbf{C}}^{k+1}_{\mathbf{1},n+1}|| \leq tol\right)$ then
        exit
    end if
end for
$\dot{\mathbf{C}}_{\mathbf{1},n+1} = \dot{\mathbf{C}}^{k+1}_{\mathbf{1},n+1}$
$\mathbf{C}_{\mathbf{1},n+1} = \mathbf{C}^{k+1}_{\mathbf{1},n+1}$
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Finally, we calculate the coupled nonlinear system (18)-(21) (second stage) solutions at t^{n+1}, taking into account C_1 and C_2 given by the first stage, and using the fourth-order Runge-Kutta integration scheme. It is well-known that this methodology is very precise to solve nonlinear ordinary differential system and it was successfully used by Odencrantz et al. (1993) to handle Monod biodegradation reaction in an operator splitting scheme. As mentioned before here the Runge-Kutta scheme also involves the evaluation of biodegradation processes as well as the sorption in equilibrium and non-equilibrium conditions, both considered nonlinear. Let n_{RK} be the Runge-Kutta number of iterations; then, the reactive time step Δt_R is calculated as $\Delta t_R = \Delta t/n_{RK}$. Consequently, the reactive time steps are considered much smaller than those used for the transport process . In the following numerical simulations we keep $n_{RK} = 50$ and vary the Δt values.

5 NUMERICAL SIMULATIONS

In this section some computational aspects related to the performance of the FC and OS numerical schemes will be carried out. In order to choose the most appropriated approach to handle with some particular nonlinear contaminant transport problems we shall study three scenarios, namely:

- scenario 1: a linear convective-diffusive single species transport problem undergoing first-order biodegradation kinetic and sorption in equilibrium mode (retardation);
- scenario 2: a nonlinear convective-diffusive two species (the acceptor and the electron donors) transport problem undergoing biodegradation given by the minimum-rate Monod kinetic;
- scenario 3: a nonlinear convective-diffusive single species transport problem undergoing non-equilibrium sorption mode given by the Freundlich isotherm.

To allow more precise comparisons both methodologies are solved via the Crank-Nicolson method applied to the temporal approximation. Besides, in the FC iterative scheme, the approximate solution of each variable in the iteration k will be evaluated using the update solutions of the variable already resolved in the same iteration.

5.1 Scenario 1

In this first scenario it will be verified the influence on the approximate solution due to the order of resolution of the OS stages, the introduction of decomposition errors and its decreasing associated to time step size reductions. For doing this, the following simplified linear diffusive-convective-reactive transport problem (scenario 1) will be considered, that is:

$$\frac{\partial F(C_1)}{\partial t} + V\frac{\partial C_1}{\partial x} - D\frac{\partial^2 C_1}{\partial x^2} + R_1(C_1) = 0, \tag{31}$$

$$R_1(C_1) = k_1^1 C_1, \tag{32}$$

where $\Phi(C_1) = K_d C_1$ in $F(C_1) = C_1 + \Phi(C_1)$ (Eq. (5)). In addition to the OS approach defined in last section (here denominated as "transport+reaction"), two new OS schemes will be introduced to show the influence on the approximate solution associated with the OS stages resolution order. Firstly, we solve the reaction part and then it is used as the initial condition to evaluate the transport problems (defined as "reaction+transport"); secondly, we interchange the problem resolution order in each time step (defined as "alternate"), that is, in the odd time steps the "transport+reaction" approach is solved and in the even time steps the "reaction+transport" method is employed. These three methodologies will be compared with a reference solution of system (31)-(32) (Valocchi and Malmstead , 1992; Morshed and Kaluarachchi , 1995; Kaluarachchi and Morshed , 1995) (defined as "refer").

Tables 1 and 2 show the data (Celia et al. , 1989; Kacur et al. , 2005; Odencrantz et al. , 1993; Remesikova , 2004, 2007) to the numerical results plotted in Figures 1 and 2.

L	$C_1(0,t)$	$C_1(x,0)$	$\frac{\partial C_1(L,0)}{\partial x}$	K_d
$15.0\,m$	$1.0\,mg\,L^{-1}$	$0.0\,mg\,L^{-1}$	$0.0\,mg\,L^{-1}\,m^{-1}$	1

Table 1: Model parameters for problem (31)-(32).

Remembering that Pe and Co are the grid Péclet and Courant numbers, defined as $Pe = |V|\Delta x/2D$ and $Co = |V|\Delta t/2\Delta x$, respectively. Thus, setting $\Delta t = 0.025$, 0.0125 and 0.001 days and considering the discretization and physical parameters given in Table 2 we have $Co = 0.5,\ 0.25,\ 0.02$, and $Pe = 0.25,\ 2.5$.

Figures	Δx	D	V
Fig. 1	$0.5\,m$	$20.0\,m^2day^{-1}$	$20.0\,mday^{-1}$
Fig. 2	$0.5\,m$	$0.2\,m^2day^{-1}$	$2.0\,mday^{-1}$

Table 2: Discretization and physical parameters for problem (31)-(32).

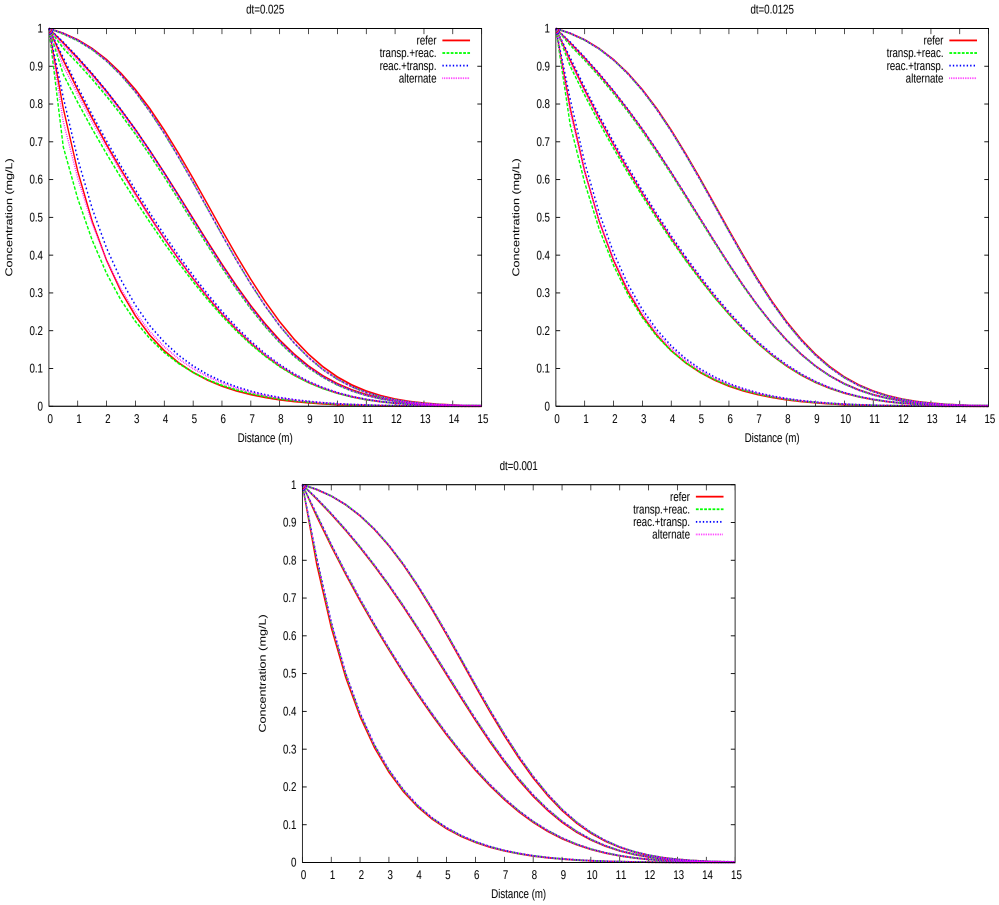

Figure 1: Contaminant concentration curves to $Pe = 0.25$ at $t = 0.5$ day corresponding to $k_1^1 = 14$, 4, 1.4 and $0.14\,day^{-1}$ (from left to right). Comparison among the reference solution and three OS procedures: $\Delta t = 0.025$ (top left), $\Delta t = 0.0125$ (top right) and $\Delta t = 0.001$ (bottom).

Contaminant concentration curves for a diffusive problem ($Pe = 0.25$) and a predominant convective one ($Pe = 2.5$) are plotted in Figs. 1 and 2, respectively, to three different time steps ($\Delta t = 0.025$, 0.0125 and 0.001 days) and four first-order biodegradation constants ($k_1^1 = 14$, 4, 1.4 and $0.14\,day^{-1}$). For both situations the OS "alternate" scheme converges faster to the reference solution. Although, it is possible to note an error due to the operator decompositions that is associated with the k_1^1 values: the higher the value of constant k_1^1, the higher is the error.

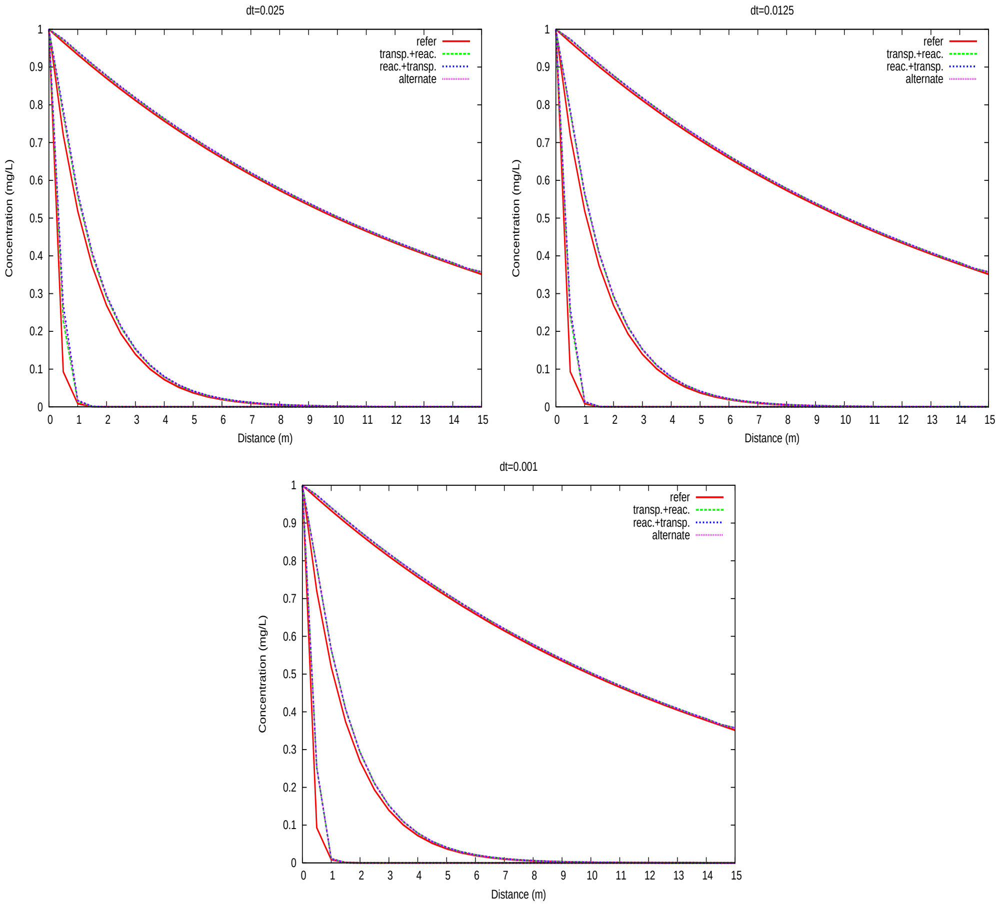

Figure 2: Contaminant concentration curves to $Pe = 2.5$ at $t = 20$ days corresponding to $k_1^1 = 14$, 4, 1.4 and $0.14\, day^{-1}$ (from left to right). Comparison among the reference solution and three OS procedures: $\Delta t = 0.025$ (top left), $\Delta t = 0.0125$ (top right) and $\Delta t = 0.001$ (bottom).

In addition, we observe the convergence of all approximate solutions to the reference solution when Δt goes to zero.

$k_1^1\ day^-1$	transp.+reac.	reac.+transp.	alternate
0.14	2.4375	2.675	2.9375
1.4	2.1625	2.5878	2.9625
14	2.4	2.4875	2.925

Table 3: Execution times (sec) for the three OS approaches plotted in Fig. 2 (down) with $\Delta t = 0.001\ day$ at $t = 20\ days$.

Finally, Table 3 presents comparisons among CPU execution times (sec) for the three OS approaches plotted in Fig. 2 (bottom). The data were obtained after executing the complete code run, calculating at $t = 20\ days$. The proposed OS approach (first-column) gives the smallest CPU time comparing with the two other schemes.

5.2 Scenario 2

In this scenario we simulate a nonlinear convective-diffusive two species (the acceptor and the electron donors) transport problem undergoing biodegradation given by the minimum-rate

Monod kinetics. The mathematical model (1)-(4) is now given by

$$\frac{\partial C_1}{\partial t} + V\frac{\partial C_1}{\partial x} - D\frac{\partial^2 C_1}{\partial x^2} + R_1(C_1, C_2, b_1) = 0, \tag{33}$$

$$\frac{\partial C_2}{\partial t} + V\frac{\partial C_2}{\partial x} - D\frac{\partial^2 C_2}{\partial x^2} + R_2(C_1, C_2, b_1) = 0. \tag{34}$$

Here the functions $R_i(\cdot,\cdot,\cdot)$, $i = 1,\ 2,\ 3$, describing minimum-rate Monod kinetics are defined by

$$R_1(C_1, C_2, b_1) = (1-\gamma)K_1(C_1) + \gamma\frac{Y_{C_2}}{Y_{C_1}}K_2(C_2), \tag{35}$$

$$R_2(C_1, C_2, b_1) = \gamma K_2(C_2) + (1-\gamma)\frac{Y_{C_1}}{Y_{C_2}}K_1(C_1), \tag{36}$$

$$R_3(C_1, C_2, b_1) = (1-\gamma)Y_{C_1}K_1(C_1) + \gamma Y_{C_2}K_2(C_2) - mb_1, \tag{37}$$

$$K_j(C_j) = \frac{V_m^1(C_j)b_1C_j}{(K_h^1(C_j) + C_j)},\ j = 1, 2. \tag{38}$$

where

$$\gamma = \gamma(C_1, C_2) = \begin{cases} 0 \text{ if } C_1 < C_2 \\ 1 \text{ if } C_2 \leq C_1, \end{cases} \tag{39}$$

with $V_m^1(C_j)$, $K_h^1(C_j)$, Y_{C_j} and m, respectively, the specific maximal degradation rate, the half-saturation concentration and the biomass yield coefficient, the biomass decrease coefficient. Finally, function $\gamma(\cdot,\cdot)$ determines who is the limiting species according to expression (39).

Considering very refined spatial and temporal grids ($\Delta x = 0.1\,m$ and $\Delta t = 0.001\,day$) the FC approximate solution is used as a ”exact" in the following numerical simulations where it is checked against the three OS schemes defined before. All numerical simulations of problem (33)-(34) were obtained with the following boundary and initial conditions: $C_1(0,t) = 10\,mgL^{-1}$, $C_2(0,t) = 3\,mgL^{-1}$, $C_1(x,0) = 0\,mgL^{-1}$, $C_2(x,0) = 3\,mgL^{-1}$ and a constant value $b_1 = 0.2\,mgL^-1$ to the bacterial biomass. The physical and discretization parameters are showed in Tables 4 and 5, respectively.

$V_m^1(C_1)$	$V_m^1(C_2)$	$K_h^1(C_1)$	$K_h^1(C_2)$	Y_{C_1}	Y_{C_2}
$1.0\,day^{-1}$	$1.0\,day^{-1}$	$0.1\,mgL^{-1}$	$0.1\,mgL^{-1}$	0.125	0.25

Table 4: Model parameters for problem (33)-(34).

L	Δx	Δt	V	D	Pe	Co	Ne	$nnode$
$100.0\,m$	$0.5\,m$	$0.5\,day$	$1.0\,mday^{-1}$	$0.2\,m^2day^{-1}$	1.25	0.5	200.0	201.0

Table 5: Discretization parameters for problem (33)-(34).

Figures 3 and 4 exhibit the electron and acceptor donors concentration curves behaviors, respectively, at $t = 17$ days (left) and $t = 68$ days (right) obtained to all three OS methods and the FC methodology.

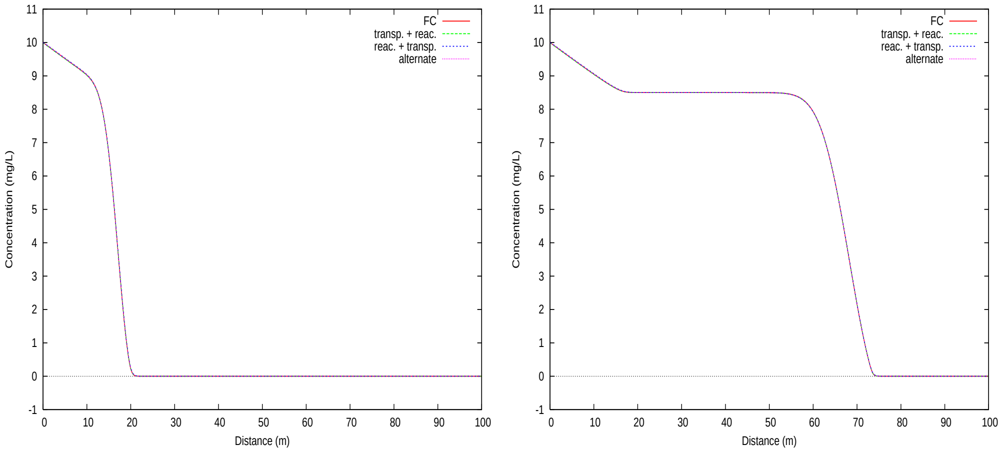

Figure 3: Electron donor concentration curves at $t = 17$ days (left) and $t = 68$ days (right). Comparison among the fully coupled method (FC) and the three operator splitting (OS) approaches.

The OS schemes present numerical approximations with the same accuracy as showed by those obtained via the FC methodology that are considered the most precise. We have still observer that biodegradation terms are not dominant in the reactive flow transport in porous media. In general, the biodegradation Monod kinetic parameters are small and they can favor the operator splitting convergence (Morshed and Kaluarachchi , 1995).

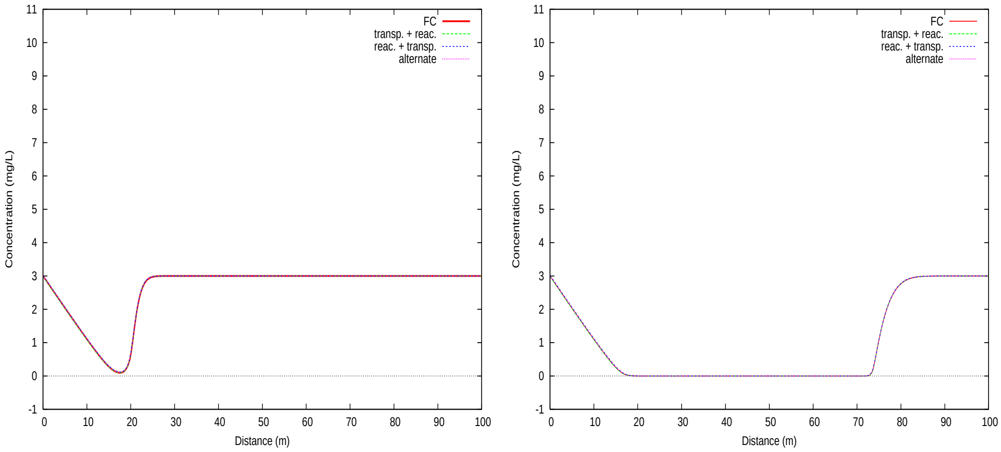

Figure 4: Electron acceptor concentration curves at $t = 17$ days (left) and $t = 68$ days (right). Comparison among the fully coupled method (FC) and three operator splitting (OS) approaches.

5.3 Scenario 3

In this last scenario we analyze a nonlinear convective-diffusive single species transport problem, which involves the aqueous and solid concentrations C_1 and S_1, respectively. To this end, the transport model system (1)-(4) becomes:

$$\frac{\partial C_1}{\partial t} + V\frac{\partial C_1}{\partial x} - D\frac{\partial^2 C_1}{\partial x^2} + \frac{\partial S_1}{\partial t} = 0, \tag{40}$$

$$\frac{\partial S_1}{\partial t} = K(\Psi(C_1) - S_1). \tag{41}$$

Next, we compare approximate solutions obtained via FC and OS approaches when applied to the transport problem (40)-(41) considering nonlinear Freundlich isotherm $\Psi(C_1) = C_1^{0.75}$ (Eq. 6) with non-equilibrium reaction constant values $K = 1$, 10, 100 and 1000, as plotted in Fig. 5 with $\Delta x = 0.01$ and $\Delta t = 0.001$. It is well known that the non-equilibrium sorption condition (see Eq. (41)) tends to a quasi-equilibrium sorption mode when K is sufficiently large ($K \mapsto \infty$) (Kacur et al. , 2005; Kanney et al. , 2003a,b; Remesikova , 2004, 2007) leading to the equilibrium sorption behavior studied in subsection 5.1 (scenario 1). As K varies from 1 to 100 both methodologies approximate the equilibrium and non-equilibrium modes. Although, for $K = 1000$, the expected physical behavior is better represented by the OS numerical result, as depicted at the right hand side of Fig. 5.

Finally, still in the quasi-equilibrium mode case ($K = 1000$), we note the numerical results convergence (see Fig. 6) when we compare the FC approach calculated with a fine grid ($\Delta x = 0.002$) and the OS method with a coarse grid ($\Delta x = 0.01$). Hence, the OS methodology produces accurate approximate solutions with no need of a refined spatial discretization.

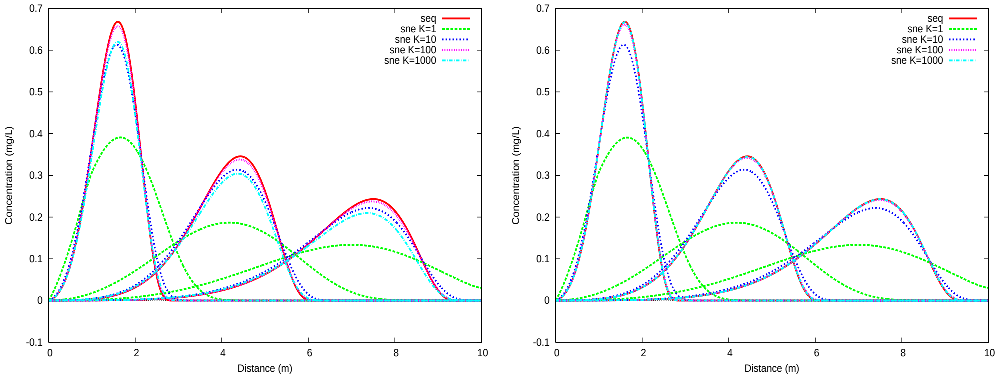

Figure 5: Contaminant concentration curves at 2, 8 and 15 days (from left to right). Comparison among sorption in equilibrium (seq) and non-equilibrium mode (sne) with $K = 1$, 10, 100 and 1000, obtained via FC (left) and OS (right) approaches.

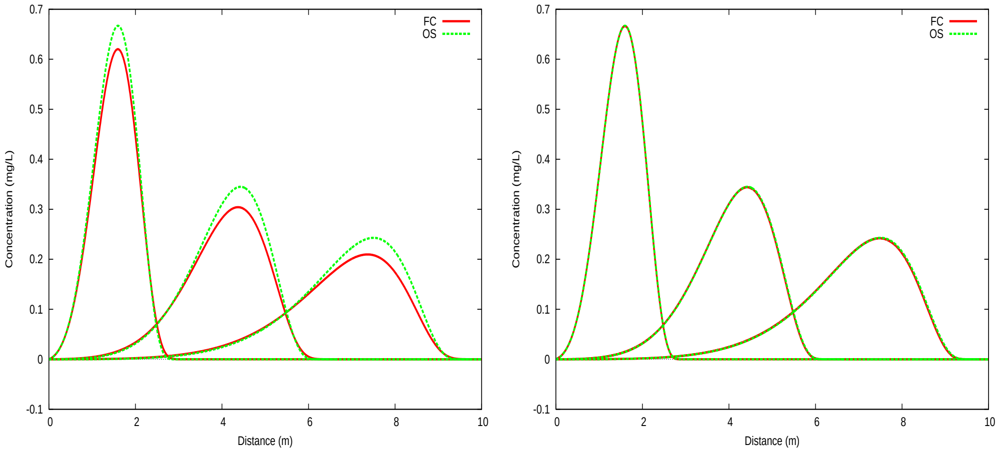

Figure 6: Contaminant concentration curves at 2, 8 and 15 days (from left to right). Comparison between sorption in non-equilibrium mode ($K = 1000$) obtained via FC and OS with $\Delta x = 0.01$ (left) and FC with $\Delta x = 0.002$ and OS with $\Delta x = 0.01$ (right).

6 CONCLUSIONS

In this paper two finite element approaches for solving multi-species contaminant transport problems undergoing the presence of sorption and biodegradation processes in a subsurface environment, which characterizes a stage of subsurface contamination by organic contaminants were studied. A fully coupled (FC) technique and an operator splitting (OS) approach were proposed in order to numerically solve three typical contaminant scenarios given by transport problems, with mass transfer between solid and aqueous phases, and nonlinear biodegradation and sorption reactions, in a one-dimensional saturated porous medium. For both methodologies the SUPG (Streamline Upwind Petrov-Galerkin) stabilized finite element method (Brooks and Hughes , 1982) in space and a predictor-multi corrector algorithm in time are used to approximate the predominant convective transport equations.

Some numerical comparisons were developed in order to analyze the efficiency and accuracy for both proposal methodologies. In fact, the OS approach implementation is the most simple with respect to the treatment of different reaction terms. Hence, its application is very attractive for parallel computation, large multidimensional problems with multiple species, treating in a novel way different types of biodegradation kinetics and sorption conditions as we have seen through the numerical results showed by scenarios 2 and 3.

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