

CONTAMINANT TRANSPORT IN POROUS MEDIA UNDER BIODEGRADATION AND NON-EQUILIBRIUM SORPTION REACTIONS

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Abstract. This paper presents an analysis of multiple species transport in saturated porous media under multiplicative Monod biodegradation kinetic and non-equilibrium sorption given by Freundlich isotherm. The problem is modeled with nonlinear system of partial differential equations coupled through sorption and biodegradation terms. The operator splitting technique was employed to approximate the problem solution in two steps: initially the advection-dispersion transport problem for the contaminant and oxygen were solved. Then, employing this first step approximation as initial condition we solved the ordinary differential equations for reactions. The finite element method and Crank-Nicolson scheme were respectively used in the spatial and time discretization of the first step. The differential equations for the reactions were approximated by fourth-order Runge-Kutta method. Applications for 1D problems were compared with other solutions obtained in the literature and some 2D results were also considered. Numerical results obtained in this work are in good agreement with solutions presented by other authors. These results allow us to verify that the biodegradation process, and consequently the biomass growth, is highly affected by non-equilibrium sorption.

1 INTRODUCTION

Groundwater has common use for supply several demands and contamination of this resource generates large concern related with public health and environmental conservation. When incidents induce soil and/or aquifer contamination a wide range of techniques can be employed [Andrade et al. \(2010\)](#). Although there are efficient techniques for recovery of affected areas the monitoring and forecasting of contaminants behavior in subsurface are needful requirements to avoid extraction and consumption of contaminated water.

Contaminant motion in porous media obeys, mainly, mechanisms of advection and hydrodynamic dispersion [de Marsily \(1986\)](#). If one considers the transport of organic contaminants, their concentration can also vary due to biological reactions [Barry et al. \(2002\)](#). Besides that, another important phenomenon to be considered is the sorption/desorption (generally called only of sorption) [Odencrantz \(1991\)](#).

Biodegradation is a organic matter transformation process mediated by bacteria or other biological organism that can provide the completely mineralization of organic contaminants or even diminish their toxicity and mobility. This usually occurs spontaneously, but can be stimulated to promote a fast contaminant decay. Among remediation techniques those based on biological reactions (bioremediation) are widely used for remediation of sites contaminated by organic compounds [Andrade et al. \(2010\)](#). Therefore, biodegradation reactions should be considered in models for the prevision of contaminant plume displacement in soils and aquifers [Bear and Cheng \(2010\)](#).

The sorption phenomenon, i.e., solute mass exchange in the interface between phases in porous media, induces delays during the transport [Serrano \(2001, 2002\)](#); [Maus et al. \(2010\)](#). Although many kinds of sorption/desorption can be distinguished in soils and rocks, two broad categories, adsorption and absorption, are normally differentiated. In adsorption, solute accumulation is generally restricted to a surface between the solution and the solid phase. In contrast, absorption is a process in which the solute interpenetrates the solid phase [Weber Jr et al. \(1991\)](#).

Some studies using computational modeling have been conducted to understand the behavior of contaminants in porous media. However, many of these works did not consider the simultaneous interactions between different reactions in the system. For instance, one can find models considering only biodegradation in [Sun and Clement \(1999\)](#); [Gallo and Manzini \(2001\)](#); [Curtis \(2003\)](#); [Bell and Binning \(2004\)](#) or only sorption in [Farthing et al. \(2006\)](#); [Frolkovic and Kacur \(2006\)](#). Others studies combine linear sorption and nonlinear biodegradation kinetics can be seen in [Gallo and Manzini \(1998a,b\)](#); [Cheyys et al. \(2010\)](#); [Sun et al. \(1998\)](#). Few works treat the coupling among nonlinear sorption and nonlinear biodegradation kinetics as it was studied by [Couto \(2006\)](#); [Couto and Malta \(2008\)](#) for the unidimensional case and bidimensional by [Maus \(2011\)](#).

Nonlinear reactions of sorption and biodegradation combined in the transport equation are addressed here. This problem is modeled as a nonlinear system of partial differential equations (PDE's) coupled through reactions terms. In our model were employed three species: organic contaminant (electron donor), oxygen (electron acceptor) and the aerobic microorganisms (biomass).

The operator splitting technique was applied to approximate the problem solution in two steps. In the first stage only the advection-dispersion problem for contaminant and oxygen are solved and in a second step we solved the ordinary differential equations (ODE's) system for the reactions terms. The finite element method and Crank-Nicolson scheme were, respectively

used for the spatial and time discretization of the first step. The reactions ODE's system were approximated by the fourth-order Runge-Kutta method. Applications with unidimensional flux were compared to other solutions obtained in the literature [Couto \(2006\)](#); [Couto and Malta \(2008\)](#) and some two-dimensional flux problems were also analyzed.

A discussion about multiple species transport at saturated porous media is presented, based on numerical solutions achieved for 1D and 2D fluxes. The main issue is to understand the organic contaminant behavior, considering their interactions with oxygen and the biomass through the biodegradation reaction and, simultaneously, undergoing sorption reaction.

2 MODELING

Soil and rocks (porous media) are structures with void spaces that can be filled with fluids such as water, air and oil among others. For the domains considered in our model there are two phases: solid matrix and water, and we assume here that all voids spaces are filled with water (saturated). We also admit that only three species are present in the domain: contaminant, oxygen and biomass. The latter is only present on the solid phase (adhered to the solids surface) while oxygen occurs only in fluid phase (dissolve oxygen), in other words, the oxygen is not sorbed by the solid phase [Couto \(2006\)](#). The contaminant here is present in both phases and can have their mass exchanged between solid and fluid phases [Odencrantz \(1991\)](#). In the next subsections we define the mathematical models used to represent the mechanisms involved in this problem.

2.1 Sorption

There is a variety of sorption models applicable in porous media, however, the most commonly used are local equilibrium model and first-order model [Barry et al. \(2002\)](#). The main feature that differentiate these models is the rate at which the mass distribution equilibrium is reached. In equilibrium model, mass equilibrium in both phases is reached instantaneously while for the first-order model (non-equilibrium model) mass equilibrium in both phases is time dependent, not occurring instantaneously [de Marsily \(1986\)](#); [Weber Jr et al. \(1991\)](#). Non-equilibrium model, equation (1), is represented as a contaminant mass variation in the solid phase.

$$\frac{\partial S}{\partial t} = K (\rho_s F(C) - S) \quad (1)$$

where C and S are the contaminant concentration in the fluid phase and in the solid phase [$M L^{-3}$], respectively. ρ_s is the density of solids [$M L^{-3}$] and the constant K is a kinetic coefficient of mass exchange among phases [T^{-1}]. This equation includes the equilibrium model description expressed by the first term on the right side. Normally it is accepted that subsurface systems have constant temperature what makes the equilibrium models to be called of sorption isotherms. A wide range of isotherms can be employed as shown in [van Genuchten and Simunek \(1996\)](#), and among those the linear (2) and Freundlich (3) are the most used.

- *Linear model:*

$$F(C) = k_d C \quad (2)$$

where k_d is a distribution/partition coefficient [$L^3 M^{-1}$], representing the equilibrium concentration among phases [de Marsily \(1986\)](#).

- Freundlich model:

$$F(C) = k_f C^{p_f} \quad (3)$$

where k_f is the Freundlich capacity coefficient [$L^{3p_f} M^{-p_f}$] and p_f is the Freundlich sorption energy dimensionless coefficient Barry et al. (2002), generally reported in the literature between 0.7 and 1.8 Barry and Bajracharya (1995). When $p_f = 1.0$ the coefficient k_f is equivalent to k_d and the model becomes a linear model.

2.2 Biodegradation

To model biologic reactions we assume here that most of the living microorganisms are adhered to solids grain Barry et al. (2002); Odencrantz (1991); Brusseau et al. (1999). Furthermore under macroscopic viewpoint there is no need to consider the distribution of organisms in the grain solids surface. The microorganisms are in direct contact with dissolved substrates. The kinetic of biological reaction is given by multiplicative Monod model equations, namely (4)-(6).

$$R_1(C, O, B) = \mu_m B \left(\frac{C}{H_C + C} \right) \left(\frac{O}{H_O + O} \right) \quad (4)$$

$$R_2(C, O, B) = \frac{Y_C}{Y_O} R_1(C, O, B) \quad (5)$$

$$R_3(C, O, B) = Y_C R_1(C, O, B) - m(B - B_0) \quad (6)$$

In these equations O and B are the oxygen concentration in the fluid phase and biomass concentration in the solid phase [$M L^{-3}$], respectively, the maximum specific degradation rate [T^{-1}] is μ_m , H_C and H_O are the half-saturation constant for the contaminant and oxygen [$M L^{-3}$], Y_C and Y_O are the biomass yield coefficients (dimensionless) and m represent the biomass decay coefficient [T^{-1}]. The initial biomass concentration is B_0 and in this multiplicative Monod kinetics both substrates (contaminant and oxygen) contribute for control biomass growth noticing that by these equations the biomass concentration is never lower than B_0 .

2.3 Reactive transport in porous media

Coupling the advective-diffusive equations (hydrodynamic flux) with biodegradation and sorption reactions we can represent the reactive transport of multiple species in porous media obtaining the following system of equations:

For contaminant:

$$\phi \frac{\partial C}{\partial t} + (1 - \phi) \frac{\partial S}{\partial t} + \mathbf{v}_d \cdot \nabla C - \nabla \cdot (\mathbf{D} \nabla C) = -\phi R_1(C, O, B) \quad (7)$$

$$\frac{\partial S}{\partial t} = K (\rho_s F(C) - S) \quad (8)$$

For oxygen:

$$\phi \frac{\partial O}{\partial t} + \mathbf{v}_d \cdot \nabla O - \nabla \cdot (\mathbf{D} \nabla O) = -\phi R_2(C, O, B) \quad (9)$$

For biomass:

$$\frac{\partial B}{\partial t} = R_3(C, O, B) \quad (10)$$

Where ϕ is the total porosity (dimensionless), \mathbf{v}_d is the Darcy velocity [$L T^{-1}$] given by the average velocity of the fluid in the porous media (\mathbf{v}) [de Marsily \(1986\)](#), as

$$\mathbf{v}_d = \phi \mathbf{v} \quad (11)$$

Assuming that advective flux is uniform and oriented in the x direction, the hydrodynamic dispersion tensor is,

$$\mathbf{D} = \begin{bmatrix} D_L & 0 \\ 0 & D_T \end{bmatrix} \quad (12)$$

with longitudinal (D_L) and transversal (D_T) components given by:

$$D_L = \phi d + \beta_L |\mathbf{v}_d| \quad (13)$$

$$D_T = \phi d + \beta_T |\mathbf{v}_d| \quad (14)$$

where d is a molecular diffusion coefficient [$L^2 T^{-1}$]. β_L and β_T are known as intrinsic dispersivity [L] in longitudinal and transversal directions of the fluid flux.

2.4 Numerical approximation

The problem we have here is a nonlinear system of partial differential equations coupled through sorption and biodegradation terms. Due to the difference in time scales between reaction and advection-dispersion problems, an operator splitting technique was applied to solve it. In this technique the approximate solution is obtained in two steps which can be solved with different timestep, as illustrated in Figure 1.

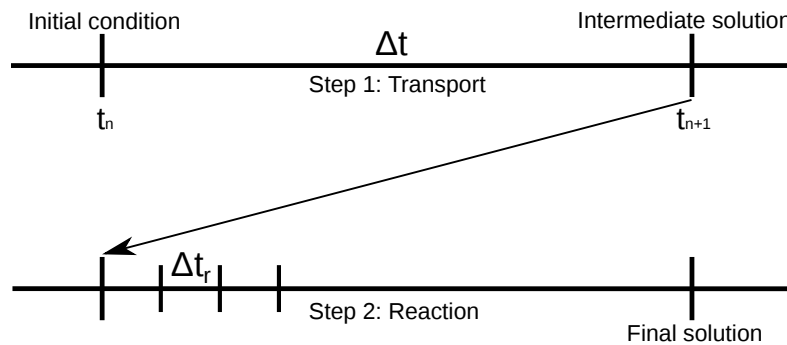


Figure 1: Scheme of operator splitting used here (adapted from [Odencrantz \(1991\)](#)).

In the first step only the advection-dispersion problems for contaminant and oxygen were solved (equations (15-16)), using a timestep of Δt . Next, in the second step, the system of ordinary differential equations (ODE's) for reactions (equation (17- 20)) were solved using the new values obtained by the intermediate solution of the first step (see Figure 1). Due to time scale of the reactions, in this second stage of the solution a much more refined timestep, $\Delta t_r (= \Delta t/N_r)$ is needed. Below are shown the equations solved in each step.

Step 1: Transport

$$\phi \frac{\partial C}{\partial t} + \mathbf{v}_d \cdot \nabla C - \nabla \cdot (\mathbf{D} \nabla C) = 0 \quad (15)$$

$$\phi \frac{\partial O}{\partial t} + \mathbf{v}_d \cdot \nabla O - \nabla \cdot (\mathbf{D} \nabla O) = 0 \quad (16)$$

Step 2: Reactions

$$\frac{\partial C}{\partial t} = - \left(\frac{(1 - \phi)}{\phi} \frac{\partial S}{\partial t} + R_1(C, O, B) \right) \quad (17)$$

$$\frac{\partial S}{\partial t} = K (\rho_s F(C) - S) \quad (18)$$

$$\frac{\partial O}{\partial t} = -R_2(C, O, B) \quad (19)$$

$$\frac{\partial B}{\partial t} = R_3(C, O, B) \quad (20)$$

where $R_1(C, O, B)$, $R_2(C, O, B)$ and $R_3(C, O, B)$ are given by multiplicative Monod kinetics, equations (4), (5) and (6), respectively.

The finite element method, with bilinear quadrilateral elements, and Crank-Nicolson scheme are respectively used in the spatial and time discretization of the first step. The ODE's system of reactions is approximated by the fourth-order Runge-Kutta method.

2.5 Simulations

Two scenarios were considered, both with rectangular domains (Figure 2). For the first one we took $x \in [0, 6]$ and $y \in [0, 1]$, and on the second we adopted $x \in [0, 20]$ and $y \in [0, 6]$. Initial conditions and boundary conditions for simulations are shown in Figure 2, except for the boundary condition at left side of the domain ($x = 0$) all other boundary conditions were the same in each case. These simulation scenarios represent, initially, a subsurface environment with an initial aerobic organisms concentration of 0.427 mg l^{-1} fully contaminated with 5.0 mg l^{-1} of some organic contaminant. Although, the organisms are in contact with the contaminant there is no oxygen, thereby, initially, biodegradation does not happen.

The same parameters of multiplicative Monod kinetics were used in both scenarios. They were: the maximum specific degradation rate $\mu_m = 0.42 \text{ day}^{-1}$, half-saturation constants $H_C = 0.218 \text{ mg l}^{-1}$ and $H_O = 0.146 \text{ mg l}^{-1}$, biomass yield coefficients $Y_C = 0.678$ and $Y_O = 0.983$ and the biomass decay coefficient $m = 0.07 \text{ day}^{-1}$.

Scenario 1. The conditions of the first scenario were adopted to represent a unidimensional flux in x direction. Thus the components of hydrodynamic dispersion tensor were simplified to $D_L = \phi d$ and $D_T = 0$. Furthermore the vertical component of velocity vector was considered to be zero. Four simulations changing the sorption parameters were tested. These and others

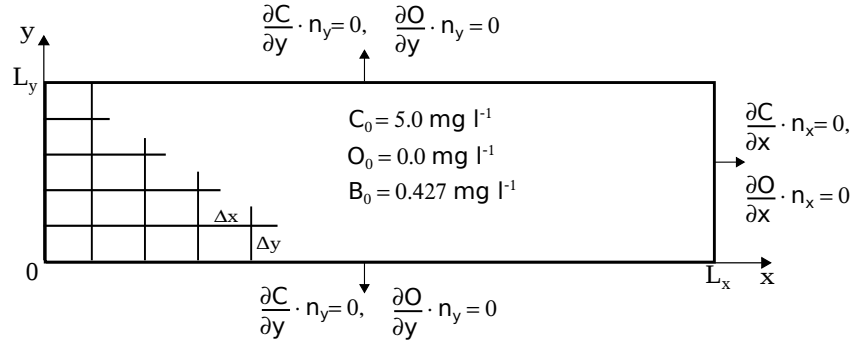


Figure 2: Domains of the scenarios.

parameters are shown in Table 1 below. For this scenario the left side ($x = 0$) boundary conditions were the following:

$$C(0, y, t) = 0, \quad y \in [0, 1], \quad t > 0 \quad (21)$$

$$O(0, y, t) = 10, \quad y \in [0, 1], \quad t > 0 \quad (22)$$

Scenario 2. For the second scenario it was considered a diffusive flux in y direction. Using this scenario two simulations changing sorption parameters were evaluated (Table 1). The boundary conditions in left side ($x = 0$) were as follows:

$$C(0, y, t) = 0, \quad y \in [0, 6], \quad t > 0 \quad (23)$$

$$O(0, y, t) = \begin{cases} 10, & y \in [0, 2] \\ 0, & \text{otherwise} \end{cases}, \quad t > 0 \quad (24)$$

Table 1: Parameters for simulations.

Parameter	Simulations for scenario 1				Simulations for scenario 2	
	1	2	3	4	5	6
p_f (-)	1.0	1.0	0.75	0.75	1.0	0.75
k_f ($\mu g g^{-1})(l mg^{-1})^{p_f}$)	2.0	2.0	2.0	2.0	0.1	0.1
K (day^{-1})	0.1	10.0	0.1	10.0	1.0	1.0
ϕ (-)	0.5	0.5	0.5	0.5	0.1	0.1
ρ_s ($g cm^{-3}$)	1.0	1.0	1.0	1.0	1.0	1.0
v_x ($m day^{-1}$)	0.05	0.05	0.05	0.05	0.009	0.009
v_y ($m day^{-1}$)	0.0	0.0	0.0	0.0	0.0	0.0
d ($m^2 day^{-1}$)	0.0003	0.0003	0.0003	0.0003	0.0001	0.0001
β_L (m)	0.0	0.0	0.0	0.0	0.06	0.06
β_T (m)	0.0	0.0	0.0	0.0	0.0005	0.0005
L_x (m)	6.0	6.0	6.0	6.0	20.0	20.0
L_y (m)	1.0	1.0	1.0	1.0	6.0	6.0
Δx (m)	0.06	0.06	0.06	0.06	0.1667	0.1667
Δy (m)	0.25	0.25	0.25	0.25	0.125	0.125
Δt (day)	0.01	0.01	0.01	0.01	1.0	1.0
Δt_r (day)	0.0002	0.0002	0.0002	0.0002	0.1	0.1

3 RESULTS

Figure 3 show the concentrations profiles for simulations 1-4. When compared with results showed by Couto (2006); Couto and Malta (2008); Odencrantz (1991), these simulations gave satisfactory results. Looking at the concentration profiles to 5 days (Figure 3), we notice a high similarity in the behavior for linear and nonlinear sorption even when the kinetic coefficient (K) is exchanged. Furthermore the smallest biological activity can be observed at 5 days.

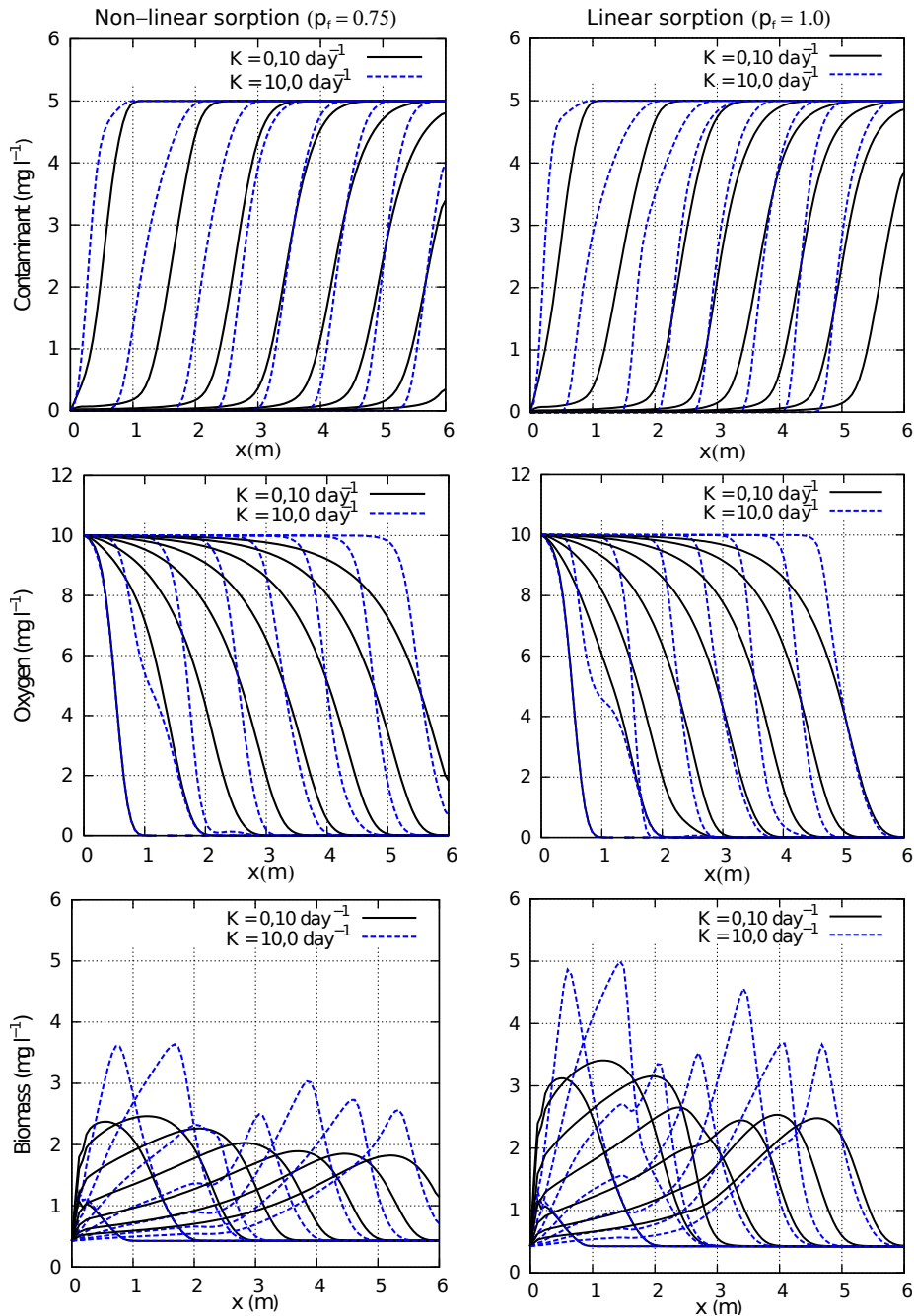


Figure 3: Longitudinal profile concentrations for simulations 1-4. Days from left to right: 5, 15, 25, 35, 45, 55, 65 e 75.

By the multiplicative Monod kinetic (equations (4-6)) the biomass growth is restricted to the presence of contaminant (electron donor) and oxygen (electron acceptor) simultaneously.

As the transport model suggest, only the contaminant is under influence of sorption, this is transported with lower velocity than oxygen, allowing that both substances remain in direct contact thus allowing biomass growth. We can observe that the largest biodegradation happens when the sorption is more intense, thereby the bigger biomass growth occurs in the simulations with $K = 10 \text{ day}^{-1}$. Simulations 2 and 4 (where $K = 10.0$) have shown a distinct behavior in the curve of 15 days which can be explained by the high biodegradation rate near this period, leading to quick oxygen consumption. Keeping K constant for different values of p_f (1.0 and 0.75) we can see that the linear sorption (simulations 1 and 2) induce a largest biomass growth because of the largest contaminant retention in the solid phase (see Figure 3).

For scenario 2 we have simulated only two values of p_f , where we tested the influence of linear sorption ($p_f = 1.0$) and nonlinear sorption ($p_f = 0.75$) under the biodegradation, keeping the kinetic coefficient $K = 0.1$ in both cases. The results produced by the simulations 5 and 6 can be viewed in the Figures 4, 5 and 6. Evolution concentration maps for contaminant, oxygen and biomass with 65 days are illustrated in the Figure 4. Evidently, when the oxygen is introduced within the contaminated region, the organic contaminant is degraded by aerobic organisms. Thus, it can be observed in the color map that biomass growth is stimulated only in front advancing of oxygen, where this is in contact with contaminant. For the time represented in Figure 4 (65 days) it was found that biomass growth of simulation 5 was higher than simulation 6, this happens because the simulation 5 employs linear sorption isotherm, consequently, the contaminant transport delay is higher. This result agrees with the results discussed above.

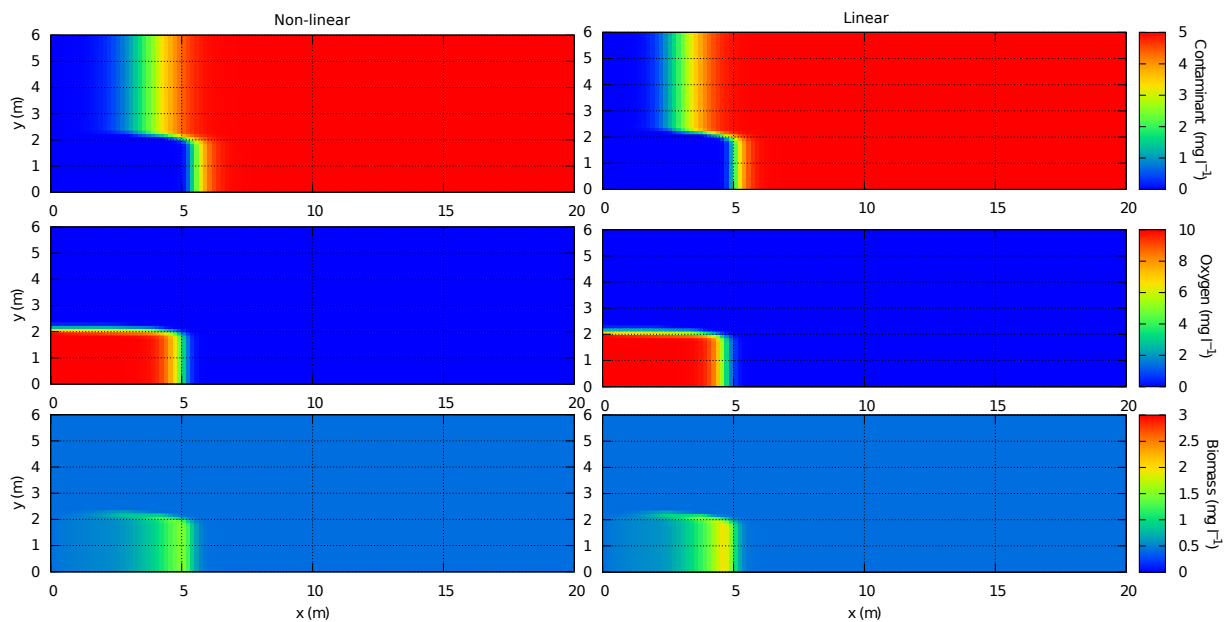


Figure 4: Map of concentrations to 65 days for simulations 5 and 6. Top to bottom: contaminant, oxygen and biomass.

For a better understanding of results graphics of concentration profile in longitudinal (Figure 5) and transversal (Figure 6) directions are presented. Thus in the Figure 5 (longitudinal profile at $y = 1$), it can be observed more clearly the difference in biomass growth, noticing that the simulation with the linear sorption model presents the largest biological activity. In the contaminant concentration profile there is a visible retardation in simulation with linear isotherm to the simulation with nonlinear isotherm. Still in Figure 5, can be viewed that also

happens a delay on the oxygen transport, but this substance is not sorbed by solid phase and the retardation is explained by the organisms respiration in biodegradation process.

In Figure 6 the transversal profile at $x = 5$ is represented. As proposed by the boundary conditions (equations (23)-(24)) the oxygen is injected for $x = 0$ at $y \in [0, 2]$ which leads to the rising in oxygen concentration firstly in $y \in [0, 2]$ (for all x). This occurs mainly due to the advective flux in direction x . The transversal profile of contaminant concentration at $x = 5$ shows that decontamination takes longer if the linear isotherm model is assumed. Moreover, as the biodegradation rate is less in simulation 5 the oxygen advances is faster than simulation 6.

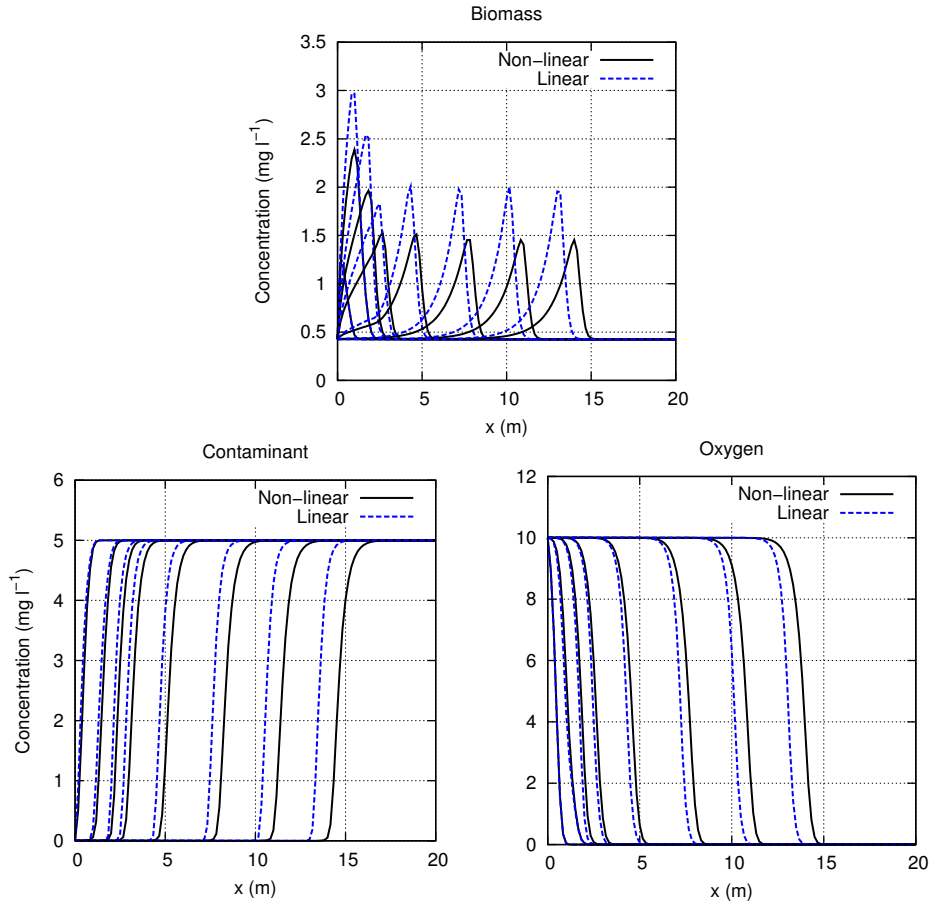


Figure 5: Longitudinal profile concentrations at $y = 1$ and $x \in [0, 20]$ for simulations 5 and 6. Days from left to right: 5, 15, 25, 35, 60, 100, 140 e 180.

4 CONCLUSIONS

Solutions here obtained indicate high influence of contaminant sorption in the biodegradation reaction and consequently over the biomass growth. For scenarios where retardation generated by sorption is high, microbiological growth also increases by virtue of the strong interaction that exists between simultaneous nonlinear reactions. This occurs because the contamination plume retardation increases the areas where the three species are present, triggering in these new areas the action of biodegradation by multiplicative Monod kinetics.

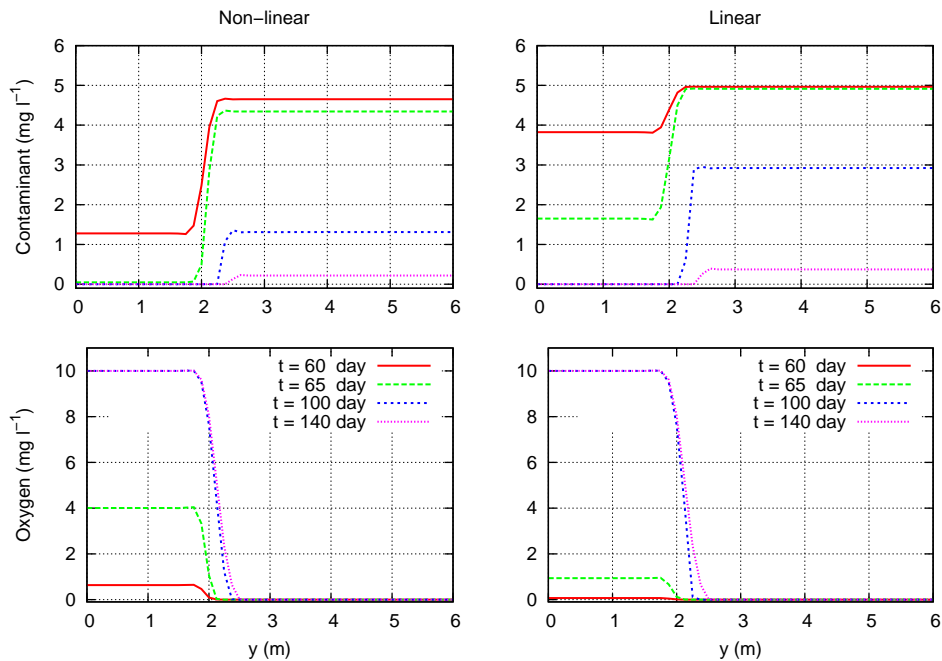


Figure 6: Transversal profile concentrations at $x = 5$ and $y \in [0, 6]$ for simulations 5 and 6.

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REFERENCES

- Andrade J.d.A., Augusto F., and Jardim I.C.S.F. Biorremediação de solos contaminados por petróleo e seus derivados. *Eclética Química*, 35:17–43, 2010.
- Barry D.A. and Bajracharya K. Optimised muskingum-cunge solution method for solute transport with equilibrium freundlich reactions. *Journal of Contaminant Hydrology*, 18:221–238, 1995.
- Barry D.A., Prommer H., Miller C.T., Engesgaard P., Brun A., and Zheng C. Modelling the fate of oxidisable organic contaminants in groundwater. *Advances in Water Resources*, 25:945 – 983, 2002.
- Bear J. and Cheng A.H.D. *Modeling groundwater flow and contaminant transport*, volume 23 of *Theory and applications of transport in porous media*. Springer, New York, NY, USA, 1 edition, 2010.
- Bell L.S.J. and Binning P.J. A split operator approach to reactive transport with the forward particle tracking eulerian lagrangian localized adjoint method. *Advances in Water Resources*, 27:323 – 334, 2004.
- Brusseau M.L., Hu M.Q., Wang J.M., and Maier R.M. Biodegradation during contaminant transport in porous media. 2. the influence of physicochemical factors. *Environmental Science & Technology*, 33:96–103, 1999.
- Cheyns K., Mertens J., Diels J., Smolders E., and Springael D. Monod kinetics rather than a first-order degradation model explains atrazine fate in soil mini-columns: Implications for pesticide fate modelling. *Environmental Pollution*, 158:1405–1411, 2010.

- Couto P.R. and Malta S.M. Interaction between sorption and biodegradation processes in the contaminant transport. *Ecological Modelling*, 214:65 – 73, 2008. Special Issue on IV Latin American Congress on Mathematical Biology.
- Couto P.R.L. *Modelagem computacional do transporte de contaminantes com processos de biodegradação e sorção física em um meio poroso saturado*. Tese de doutorado, Programa Multidisciplinar de Pós-Graduação em Modelagem Computacional do Laboratório Nacional de Computação Científica - LNCC, Petrópolis, RJ, 2006.
- Curtis G.P. Comparison of approaches for simulating reactive solute transport involving organic degradation reactions by multiple terminal electron acceptors. *Computers & Geosciences*, 29:319 – 329, 2003. Reactive Transport Modeling in the Geosciences.
- de Marsily G. *Quantitative hydrogeology: groundwater hydrology for engineers*. Academic Press, Inc., San Diego, 1986.
- Farthing M.W., Kees C.E., Russell T.F., and Miller C.T. An ellam approximation for advective-dispersive transport with nonlinear sorption. *Advances in Water Resources*, 29:657 – 675, 2006.
- Frolovic P. and Kacur J. Semi-analytical solutions of a contaminant transport equation with nonlinear sorption in 1d. *Computational Geosciences*, 10:279–290, 2006.
- Gallo C. and Manzini G. 2-d numerical modeling of bioremediation in heterogeneous saturated soils. *Transport in Porous Media*, 31:67–88, 1998a.
- Gallo C. and Manzini G. A mixed finite element/finite volume approach for solving biodegradation transport in groundwater. *International Journal for Numerical Methods in Fluids*, 26:533–556, 1998b.
- Gallo C. and Manzini G. A fully coupled numerical model for two-phase flow with contaminant transport and biodegradation kinetics. *Communications in Numerical Methods in Engineering*, 17:325–336, 2001.
- Maus V.W. *Modelagem computacional aplicada ao transporte de contaminantes em águas subterrâneas*. Dissertação de mestrado, Programa de Pós-Graduação em Modelagem Computacional da Universidade Federal de Juiz de Fora - UFJF, Juiz de Fora, MG, 2011.
- Maus V.W., Toledo E.M., and Barra L.P.S. Modelagem da dispersão de contaminantes em meios porosos com reação de sorção. In *4MCSUL - IX ERMAC*, volume 1, pages 149–154. Rio Grande RS, Brazil, pp. 149-154, 2010.
- Odenrantz J.E. *Modeling the biodegradation kinetics of dissolved organic contaminants in a heterogeneous two-dimensional aquifer*. Doctors thesis, Graduate College of the University of Illinois at Urbana-Champaign, 1991.
- Serrano S.E. Solute transport under non-linear sorption and decay. *Water Research*, 35:1525 – 1533, 2001.
- Serrano S.E. Reply to comment on "solute transport under non-linear sorption and decay". *Water Research*, 36:3171 – 3172, 2002.
- Sun Y. and Clement T.P. A decomposition method for solving coupled multi-species reactive transport problems. *Transport in Porous Media*, 37:327–346, 1999.
- Sun Y., Petersen J.N., Clement T.P., and Hooker B.S. Effect of reaction kinetics on predicted concentration profiles during subsurface bioremediation. *Journal of Contaminant Hydrology*, 31:359–372, 1998.
- van Genuchten M.T. and Simunek J. Evaluation of pollutant transport in the unsaturated zone. In *P.E. Rijtema and V. Elias (eds.), Regional Approaches to Water Pollution in the Environment, NATO ASI Series: 2. Environment, Kluwer, Dordrecht, The Netherlands*, pages 139 – 172. 1996.

Weber Jr W.J., McGinley P.M., and Katz L.E. Sorption phenomena in subsurface systems: Concepts, models and effects on contaminant fate and transport. *Water Research*, 25:499–528, 1991.