Reactive transport model coupled to multiphase flow models

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Motivation for this work is the modeling of contamination and remediation in unsaturated zone. A reactive transport model has been coupled to general multiphase flow model(s) under multiblock multiphysics simulator framework IPARS (Integrated Parallel Accurate Reservoir Simulator). In this paper we present the structure of the coupling which is a template for coupling of different models defined in overlapping computational domains. Results of the simulation demonstrate the importance of the use of multiphase flow model for simulations in unsaturated zone.

1. Introduction

With the emergence of new computational methodologies and with dramatic increases in computational power, it has become possible to formulate and to implement general multiphase multicomponent physical models driven by both energy and environmental applications in subsurface and surface flow and transport phenomena [11,17,5]. In fact, it is now widely recognized that the complexity of processes in the vadose zone requires multiphase flow models coupled to increasingly more involved models of geochemistry and transport of contaminants through sediment layers and fractures.

Unfortunately, the process of developing, and of solving, a large *tightly coupled* system describing all relevant processes at all relevant scales can be costly. Moreover, it may constrain the freedom in choosing the underlying numerical discretizations which may lead to i) unnecessary uniformity of the numerical schemes with little room for adaptivity or to ii) high computational costs or to iii) undue simplifications. As an alternative, *loosely coupled* systems are developed. These offer modularity of the coupling allowing to study the advantages and disadvantages of the individual algorithms before they are selected as building blocks of a coupled comprehensive system. In fact traditionally somewhat different techniques for spatial discretization and for time–stepping of multiphase flow models versus reactive transport models have been proposed and analyzed. The methods for the former include fully implicit, sequential or IMPES approaches [12,4]. The common technique for the latter is one of *operator-splitting* in which i) the (single-phase) flow problem is solved independently of the reactive transport equations and in which ii) reactive transport equations themselves are subject to *splitting* into the advection, reaction and diffusion steps [3,20,6]. The splitting techniques are under intense revision; moreover, different numerical techniques used for coupled or un-coupled advection/reaction/diffusion steps are now under investigation [21,19].

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The purpose of this work was to set-up a generic testbed for coupling of general multiphase flow models to reactive transport models. In this testbed different numerical models and different types of couplings can be tested. The assumptions used in the coupling are those of 1) negligible dependence of flow paths on the density and on the composition of species dissolved in flowing phases, 2) equilibrium partitioning of species between phases, 3) validity of operator-splitting techniques applied to solve the phase-summed advection-reaction-diffusion system. The testbed which we call `TRCHEM` is part of the reservoir simulator framework IPARS (Integrated Parallel Accurate Reservoir Simulator) [10,22]. IPARS models *multiphysics* phenomena in *multiblock* porous media [22], and is suitable for massively parallel computers or clusters of workstations or stand-alone PCs. The reactive transport module described below was partially ported from ParSSim [1] and extended for this work [16,14] and it is suitable for simulation of reactive transport and of remediation phenomena in unsaturated flow zones. Moreover, it can be regarded as a template for (loose) coupling of any number of models in a staggered fashion with capabilities to be extended to more tightly (iteratively) coupled approaches. Clearly a set-up of a system like `TRCHEM` is less complex than the development of a comprehensive coupled model from scratch.

On one hand, we follow [2,3] and we extend traditional single-phase flow based models of reactive transport to general multiphase compressible flow. On the other hand, our development takes advantage of the *multiblock* and *multiphysics* features of the IPARS whereby flow models can operate on different subdomains independently and for which non-matching grids can be used and which are scalable in parallel, see [22] and references therein. The extension of the multiblock features to the reactive transport is underway and it will be discussed elsewhere.

The plan of this paper is as follows. In Section 2 we briefly describe the underlying models for the flow and for reactive transport. Here for brevity we focus on two-phase flow models; however, our formulation is appropriate for any single- or multiphase flow models [16]. In Section 3 we define the time splitting algorithm and describe the structure of the coupling. Section 4 contains some numerical results obtained using `TRCHEM`.

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2. Physical Models for Multiphase Flow and Reactive Transport

2.1. Flow model

Here we consider a generic two–phase immiscible flow model. The *wetting phase* is denoted by $p = w$ and the *nonwetting phase* (oil or air) is denoted by $p = nw$. For each phase we use pressures P_p, saturations S_p, densities ρ_p, viscosities μ_p and relative permeabilities k_p [12]. The mass conservation and Darcy's law equations are

$$\frac{\partial \Phi S_p \rho_p}{\partial t} + \nabla \cdot (\rho_p \mathbf{u}_p) = q_p, \quad \mathbf{u}_p = -\mathbf{K}\frac{k_p}{\mu_p}(\nabla P_p - \rho_p G \nabla D). \tag{1}$$

Here we denote by $\Phi, \mathbf{K}, G, D$ respectively, the porosity, permeability, gravity constant and depth of the porous medium.

These equations are complemented by the volume balance $S_w + S_{nw} = 1$ and by the capillary pressure relationship $P_{nw} = P_w + P_c(S_w)$. Also, both fluid phases are assumed to

be (slightly) compressible so that $\rho_p = \rho_{p,ref} e^{c_p P_p}$. In addition, if the non-wetting phase is gaseous (for example, air), then we use some other relationship (for example, the *real gas law*) to describe $\rho_p = \rho_p(P_p)$. Also, if there is only one flowing phase (for example, water phase $p = w$), then $S_p = 1, k_p = 1$ and the system (1) is reduced. Note that Darcy's law can be replaced by some other momentum equation, for example Forchheimer's. Finally, terms q_p in equation (1) represent well (mass) rates.

2.2. Reactive Transport Equations

The mass conservation equations are written for each species α and for each stationary phase s and flowing phase p. Denote by $c_{\alpha p}$ the concentration of species α in phase p. For the flowing phases, the amount of species α accumulated in a flowing phase p per unit volume is equal to $\Phi S_p c_{\alpha p}$. Reaction terms R^I, R^C, R^N are allowed and here they are proportional to phase volume. The mass conservation equations are written as

$$\frac{\partial \Phi c_{\alpha p} S_p}{\partial t} + \sum_i \frac{\partial J_{\alpha p i}}{\partial x_i} = R^I_{\alpha p} + \Phi S_p R^C_{\alpha p} + \Phi S_p R^N_{\alpha p} + q_{\alpha p}. \tag{2}$$

Mass flux $J_{\alpha p i}$ for each flowing phase p and each species α includes contributions from advection, diffusion and dispersion as follows

$$J_{\alpha p i} = c_{\alpha p} u_{p i} - \Phi S_p \sum_j D_{\alpha p i j} \frac{\partial c_{\alpha p}}{\partial x_j}, \tag{3}$$

where diffusion/dispersion tensor $D_{\alpha p i j}$ is composed of molecular diffusion and mechanical dispersion terms. The summary definition of the aggregate diffusion/dispersion tensor is

$$\Phi S_p D_{\alpha p i j} = \left(\Phi S_p \tau_p d_{mol,\alpha p} + d_{trans,p} \left\| u_p \right\|\right) \delta_{ij} + \left(d_{long,p} - d_{trans,p}\right) \frac{u_{pi} u_{pj}}{\left\| u_p \right\|} \tag{4}$$

For each species α in each stationary phase s we have similar equation as above except there is no advective or diffusive/dispersive mass flux term.

Our main assumption follows Henry's law and it states that the partitioning of species between phases can be described by a fixed relationship $c_{\alpha p} = \Gamma_{\alpha p} c_{\alpha r}$ where r is reference phase and $\Gamma_{\alpha p}$ is a constant. In this work we assume water-wet rocks and we choose water phase as the reference phase. Alternatively, a different reference phase for each component can be specified or a *total concentration* can be used.

In order to get the phase–summed transport equation for species α in the reference flowing phase we sum the equations (2,3,4) over all flowing phases

$$\frac{\partial \Phi^*_\alpha c_{\alpha w}}{\partial t} + \nabla \cdot \left(\mathbf{u}^*_\alpha c_{\alpha w} - \mathbf{D}^*_\alpha \nabla c_{\alpha w}\right) = R^{TC}_\alpha + R^A_\alpha + R^{TN}_\alpha + q^T_\alpha \tag{5}$$

where for the two flowing phases $p = w, nw$ we define

$$\Phi^*_\alpha = \Phi\left(\Gamma_{\alpha,nw} S_{nw} + S_w\right), \quad u^*_{\alpha i} = \Gamma_{\alpha,nw} u_{nw,i} + u_{wi} \tag{6}$$

$$D^*_{\alpha i j} = \left(\Phi\left(\tau_{nw} S_{nw} \Gamma_{\alpha,nw} d_{mol,\alpha,nw} + \tau_w S_w d_{mol,\alpha w}\right)\right. \tag{7}$$

$$\left. + \left(d_{trans,nw} \left\| u_{nw} \right\| \Gamma_{\alpha,nw} + d_{trans,w} \left\| u_w \right\|\right)\right) \delta_{ij} \tag{8}$$

$$+ \left(d_{long,nw} - d_{trans,nw}\right) \frac{u_{nw,i} u_{nw,j} \Gamma_{\alpha,nw}}{\left\| u_{nw} \right\|} + \left(d_{long,w} - d_{trans,w}\right) \frac{u_{wi} u_{wj}}{\left\| u_w \right\|} \tag{9}$$

$$R^{TC}_\alpha = \Phi\left(S_{nw} R^C_{\alpha,nw} + S_w R^C_{\alpha w}\right), \quad R^{TN}_\alpha = \Phi\left(S_{nw} R^N_{\alpha,nw} + S_w R^N_{\alpha w}\right) \tag{10}$$

$$q^T_\alpha = \left(q_{\alpha,nw} + q_{\alpha w}\right). \tag{11}$$

Here we have used the fact that the net interphase transfer between flowing phases is zero $\sum_p R^I_{\alpha p} = 0$. Also, the adsorption term R^A_α is net mass transfer per porous medium volume of component α into (positive) or out of (negative) rock (all stationary phases).

The system (5) is solved for concentration of species in the reference phase $c_{\alpha w}$. Concentrations in other phases or total concentrations can then be computed through Henry's law. This system is discretized in time and in space and it is solved by *time–splitting* as shown in Section (3).

Boundary conditions. The boundary conditions relevant to `TRCHEM` module are these applied to the flow model as well as those applied to the transport-chemistry part. Specifically, boundary terms enter the equation (5) through the normal part of the advective and diffusive fluxes $(\mathbf{u}^*_\alpha c_\alpha - \mathbf{D}^*_\alpha \nabla c_\alpha) \cdot \nu$ where ν is the outward unit normal to the boundary $\partial\Omega$ of the domain Ω. Therefore, the values of $\mathbf{u}^*_\alpha$ and of c_α or of its gradient must be specified. The former quantity, $\mathbf{u}^*_\alpha \cdot \nu$ is determined directly or indirectly from the flow boundary conditions, which are handled appropriately to the applied spatial discretization [15]. Note that, in a general multiblock case, the boundary $\partial\Omega$ may be an external boundary or just a *subdomain* boundary (*interface*). In either case the flow model ensures the conservation of mass and of momentum of the flowing phases across $\partial\Omega$. Finally, the conditions on concentration c_α or on its gradient ∇c_α are subject to the time-splitting. Some delicate issues related to the extended stencil or specific spatial discretizations may arise.

Wells. The well terms q_p in flow models are defined using the Peaceman correction [13]. In the `TRCHEM` model, the wells are represented by the source-sink term q^T_α in the equation (5) and are handled in the advection step, see below. These terms are either linked to the injection/production rates of the flowing phases q_p or are pure source/sink terms of species α.

3. Numerical model

Here we discuss spatial and temporal discretizations. As we mentioned, the main feature of our work is a modular approach: the user can assign different numerical models and discretizations to multiphase flow and to reactive transport modules. Moreover, they do not need to be identical in all blocks/subdomains. In addition, even though in this work we assume that the spatial grids used by the flow and by the concentration steps are the same, this restriction is easy to be removed and then appropriate interpolation and/or projection maps are used. As concerns temporal discretization, the (multiphase) flow model is in general transient and it is solved using its own flow-specific time stepping scheme which is independent of the time stepping used by the reactive transport part.

(F) Flow time step: The flow model equations (1) are discretized in space with the use of expanded mixed finite element methods with RT_0 space, see [15] and references therein. Discretization in time at each *flow time step* $t = t^0, t^1, \ldots t^n, \ldots$ is implicit or explicit, with various solvers used to solve the resulting algebraic system [7]. Other formulations (Discontinuous Galerkin, unstructured grids) are underway. In addition, the flow model may be discretized with a multiblock multiphysics approach. See [22] and references therein.

(P) Post–processing: Consider $t \in (t^n, t^{n+1})$ and a given α. Assume that the solutions of the flow time step or values of $S_p, \mathbf{u}_p$ are available at the old $t = t^n$ and at the new flow time steps $t = t^{n+1}$ in the interior and on the boundaries, if appropriate. We compute the phase–summed values of $\Phi^*_\alpha, \mathbf{u}^*_\alpha$ etc. as in (6)-(11) at any $t \in (t^n, t^{n+1})$ by linear interpolation between old and new flow time steps.

(C) Concentration time step: Consider that at time $t = t^m$ we are given $(c^m_\alpha)_\alpha$ and that we want to take a *concentration step* that is, to compute c^{m+1}_α. The *concentration time step* in general is different (smaller) than the *flow time step* and we assume that $(t^m, t^{m+1}) \subseteq (t^n, t^{n+1})$. Denote $\triangle t^{m+1}_C = t^{m+1} - t^m$ and set $T_\alpha = \Phi^*_\alpha c_{\alpha w}$. Straightforward discretization in time of system (5) is

$$\frac{T^{m+1}_\alpha - T^m_\alpha}{\triangle t^{m+1}_C} + \nabla \cdot (\mathbf{u}^{*,m+1/2} c^m_{\alpha w} - \mathbf{D}^{*,m}_\alpha \nabla c^{m+1}_{\alpha w}) = R^{TC,m+1/2}_\alpha + R^{TN,m+1/2}_\alpha + q^{T,m+1/2}_\alpha. \quad (12)$$

Direct solution of (12) is difficult and in case of complex chemical reactions may be practically impossible even if some terms like advection are treated explicitly. For this reason, in this work we apply a further splitting of the *concentration step* in which the advection **(C.A)**, the chemistry **(C.C)**, and the diffusion/dispersion **(C.D)** subproblems are solved "independently" in the sense that they deliver intermediate values of T_α as $\overline{T}_\alpha, \widehat{T}_\alpha, T^{m+1}_\alpha$. Each may have a different numerical algorithm and discretizations assigned. Some stability and consistency restrictions may apply [20,6,3].

(C.A) Advection. We describe here the first order Godunov method but other techniques are being investigated and compared, see [21]. Set $T^m_\alpha = \Phi^{m,*}_\alpha c^m_{\alpha w}$ and compute explicitely $\overline{T}_\alpha$ from

$$\frac{\overline{T}_\alpha - T^m_\alpha}{\Delta t} + \nabla \cdot (\mathbf{u}^{*,m+1/2} c^m_{\alpha w}) = q^{T,m+1/2}_\alpha. \quad (13)$$

(C.R) Reaction Step. We solve the equation for kinetic reaction type by ODE integration explicitely

$$\frac{\widehat{T}_\alpha - \overline{T}_\alpha}{\Delta t} = R^{TC}_\alpha,$$

where the forward Euler first–order scheme has been used. This equation is an ODE and is *local* to a cell. Other schemes, for example Runge-Kutta method, can be applied.

We note that in order to account for all other types of chemical interactions, the right–hand side of this equation should contain terms $R^{TN}_\alpha + R^A_\alpha$. However, it turns out that in case of linear adsorption, the term R^A_α can be handled, instead of in the reaction step, by modifying Φ^*_α. The radionuclide decay terms R^{TN}_α can be handled, instead of in the reaction step, in the diffusion step described below. The choice is left to the user.

(C.D) Diffusion/Dispersion. Diffusion step is solved implicitly with respect to concentrations with time–lagged diffusion–dispersion tensor as

$$\frac{T^{m+1}_\alpha - \widehat{T}_\alpha}{\Delta t} - \nabla \cdot (\mathbf{D}^{*,m}_\alpha \nabla c^{m+1}_{\alpha w}) = 0. \quad (14)$$

In accordance with the above remarks, the right–hand side may include radionuclide decay terms R^{TN}_α.

For the spatial discretization, here we discuss the one based on cell–centered finite difference method with a standard 7-point stencil; other formulations are possible and are being tested [21]. The resulting linear system is not necessarily symmetric because the saturations vary in space and it is solved by GMRES with one of many preconditioners available [7]. The use of 7-point stencil solver restricts i) the use of general (full) tensor. and ii) the kind of boundary conditions that can be applied.

4. Numerical examples

Here we discuss two numerical examples. Both require the use of a two-phase flow model. See [14] for a single-phase flow example for using TRCHEM model.

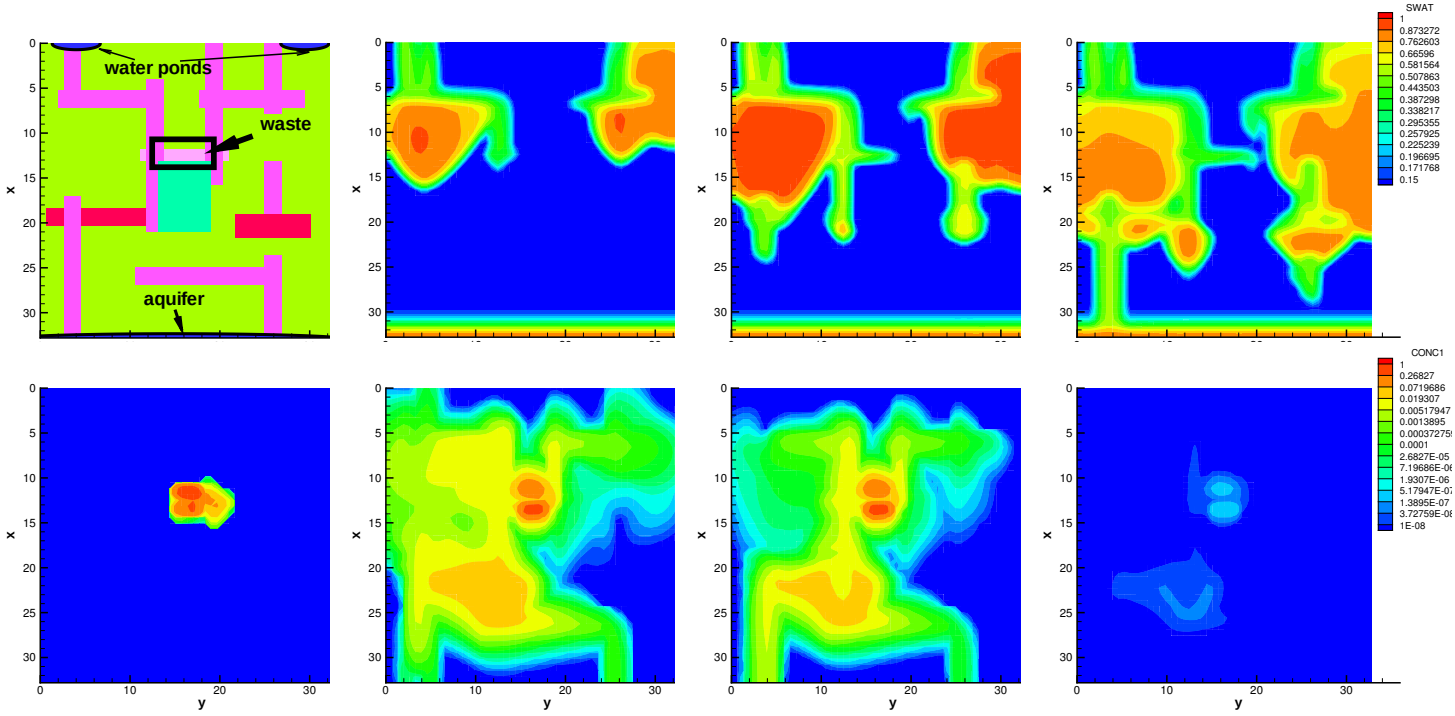

Figure 1. Top: geometry, permeability and water saturation after 4.4, 6.85 and 10 years. Bottom: concentration $[lbmol/ft^3]$ of a tracer soluble in water only, air only and in both phases (from left to right) and of the radionuclide soluble in both phases after 10 years.

4.1. Flow and reactive transport of radionuclides in vadose zone

This example is motivated by problems considered in several DOE projects, in particular, by those listed on INEL Web page www.inel.gov as well as by the planned repository in Yucca Mountain [9]. The domain is a 2D crosssection through a fractured reservoir connected to an aquifer by a boundary condition at the bottom. It is subject to periodic ponding of water on the upper surface, see Figure 1. Air is allowed to escape through parts of the upper surface. All other boundaries are no-flow. Air-water properties are taken from [11]. For lack of space we do not give details.

The flow in this reservoir occurs mainly through the system of fractures. There is a radionuclide contaminant of the half-life time comparable to the time scale of the flow

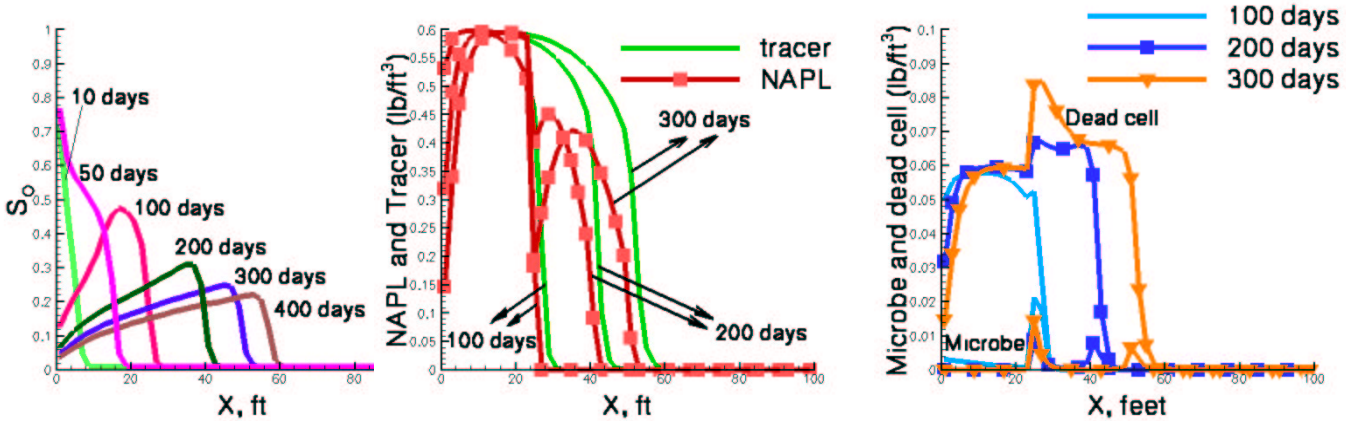

Figure 2. From left to right: 1) Biophase saturation; 2) NAPL and tracer profile; 3) Microbe population and dead cells at various times.

which has been placed in a tunnel located just above an impermeable zone. Such contaminant can be soluble in both flowing phases or only in water phase or only in air phase. The flow patterns in this case are such that in the case of only water-soluble contaminant, the plume will stay very close to its initial position because there is very little water movement around the original "hot spot" location. In other cases, the conservative tracer simulation shows that some amounts of the tracer will be transported to the groundwater. However, these concentrations may be very low in the case of radionuclide decay.

4.2. Transport and remediation of NAPL with two-phase flow

Ground pollution by petroleum products and the substantial costs involved in the remediation of such contaminated sites have led to increased interest in accurate modeling of transport and remediation of NAPL. However, most simulations assume that biophase (organic phase) is immobile. This is likely not appropriate when biophase saturation is large near the leaking location shortly after the spill. The following 1D example considers biophase as a flowing phase. Initially water-saturated media is subjected to a 50 days NAPL (xylene) spill followed by clean water flushing, both through the left boundary, see Figure 2. Fresh air comes through a remediation well located in first quarter of the domain. The biogeochemical reactions include aerobic degradation, denitrifying degradation and microbial decay. Parameters come from [18] and [8]. In addition, we consider a biochemically inactive tracer similar to NAPL.

The flow of biophase is the source of contamination. Due to lack of dissolved oxygen and nitrate, upstream behavior of NAPL and tracer are similar before the plume reaches the remediation well (at 90 days). The effect of remediation becomes significant after 200 days due to biochemistry near the well and locally downstream. The microbe population downstream from the remediation well gradually grows due to sufficient amounts of dissolved oxygen and nitrate. This results in a secondary high–spot of microbe population at 300 days.

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