Abstract  When a realistic modelling of radioactive contaminant transport in flowing groundwater is required, very large systems of coupled partial and ordinary differential equations can arise that have to be solved numerically. For that purpose, the software package \( r^3t \) is developed in which several advanced numerical methods are implemented to solve such models efficiently and accurately. Using software tools of \( r^3t \) one can treat successfully nontrivial mathematical problems like advection-dominated system with different retardation of transport for each component and with nonlinear Freundlich sorption and/or precipitation. Additionally, long time simulations on complex 3D geological domains using unstructured grids can be realized. In this paper we introduce and summarize the most important and novel features of numerical simulation for radioactive contaminant transport in porous media when using \( r^3t \).

1 Introduction

The software package \( r^3t \) (radionuclides, reactions, retardation and transport, see \[13\]) can help to simulate the spreading of radioactive contaminants in flowing groundwater. The general mathematical model that is solved numerically by \( r^3t \) describes not only the contaminant transport by advection, diffusion and dispersion, but also several reactions due to decay, sorption (kinetic and in equilibrium, linear and nonlinear), immobilisation and precipitation.

Numerical approximations used in \( r^3t \) are derived from finite volume discretization methods and they follow mass balance laws. The methods use a mixture of second and first order accurate approximations and they can produce numerical solutions without non-physical oscillations.

The package \( r^3t \) is based on the UG toolbox (Unstructured Grids, see \[3-5\]) that enables the users of \( r^3t \) to realize their numerical simulations using unstructured 2D/3D grids that can be refined and unrefined locally during computations. Moreover, parallel computations can be realized on several hardware/software platforms.

This paper gives an overview of the following topics related to software tools \( r^3t \): the general mathematical model, the implemented numerical methods, and some illustrative examples. We emphasize here the following concepts behind \( r^3t \). Firstly, the mathematical model is formulated in a general and abstract form that enables a flexible usage of \( r^3t \) for applications not restricted to contaminant transport, when the usage requires implementation of some functions and procedures in C language. Similarly, a general purpose finite volume method is implemented for a numerical solution of such mathematical model.

On the other hand, the particular application of contaminant transport in flowing groundwater is supported directly in \( r^3t \) by a possibility for users to define related physical parameters with no modifications of the code. Furthermore, a modular implementation of the general purpose finite volume method is used to include in \( r^3t \) some advanced numerical methods for specific demands of this particular application like a case of advection dominated transport or very fast decay reactions. Therefore in our description of \( r^3t \) we always proceed from a rather abstract description at the beginning to particular forms at the end.

The paper is organized as follows. In Section 2 we present the general mathematical model in an abstract
form. The most important particular cases of this model for contaminant transport and retention are described in Section 3. Furthermore, the general purpose numerical method is given in Section 4 and specific advanced methods are presented in Section 5. Numerical experiments can be found in Section 6. Finally, some conclusions are given in Section 7.

2 General mathematical model

In this section, we build a rather general mathematical model that describes in an abstract way the processes that contaminants undergo in groundwater flow in porous media. We begin with a system of partial differential equations that describes the behaviour of contaminants dissolved in flowing groundwater. Afterwards, optional extensions of the model in a form of additional (and coupled) ordinary differential equations will be given. Finally, the most typical particular case of the general model will be discussed in details.

2.1 System of PDEs

The mathematical model of transport and retention of contaminants in groundwater flow can be formulated as a system of coupled partial differential equations (PDEs) for $i = 1, \ldots, I$:

$$\Theta \partial_t (R_i c_i) + \nabla \cdot J_i = F_i,$$  \hspace{1cm} (1)

where the flux $J_i$ is defined by

$$J_i = V S_i c_i - D_i \nabla (S_i c_i).$$  \hspace{1cm} (2)

This rather abstract formulation of (1) is followed also in the implementation of all numerical approximations and methods in $r^3 t$ used to solve (1) - (2). Therefore, it enables a flexible usage of $r^3 t$ not restricted only to solve one fixed application, but allowing different implementations of coefficients $\Theta$, $R_i$, $F_i$ and $S_i$ for different applications. Nevertheless, in what follows, we concentrate on a specific description of contaminant transport in flowing groundwater where the particular form of coefficients in (1) and (2) is computed by $r^3 t$ after a set of physical parameters is defined by users, see a description in Section 2.2 later.

The unknown function $c_i = c_i(t,x)$ represents the concentration of contaminant or other species for $t \geq 0$ and $x \in \Omega \subset \mathbb{R}^d$, $d = 2$ or $d = 3$. Every coefficient $R_i$, $S_i$ and $F_i$ in (1) can depend in general on all unknown concentrations creating a fully coupled system of PDEs.

The coefficient $\Theta = \Theta(x)$ (the “water content”) characterizes the part of porous media where the flow of groundwater takes place. The vector function $V = V(t,x)$ is a given velocity field. It can be described analytically or as a numerical solution of some groundwater flow model. The effective diffusion matrix $D_i = D_i(x)$ can represent an anisotropic diffusion (in general, different for each contaminant of the system) and a dispersion tensor $[8, 13]$.

Next we describe the important role of coefficients $R_i$ in (1) and $S_i$ in (2). In the simplest case, $R_i \equiv 1$ and $S_i \equiv 1$, the function $c_i$ describes the concentration of contaminant occurring in flowing groundwater only in a single form, i.e. dissolved. Using different definitions such that $\infty > R_i > 1$ and $0 < S_i < 1$, one can conveniently model situations in which the contaminant occurs also in different forms, e.g. adsorbed and/or precipitated. Such forms of contaminant are not transported in groundwater, but they cause a retention of the transport for the dissolved part of contaminant. It is important to note that these forms must be in equilibrium with the dissolved form, i.e. their concentrations can be expressed as a function of concentrations $c_i$, see later for particular examples.

For any volume $V \subset \Omega$ of porous media the total content (mass) $M_i$ of contaminant is expressed by

$$M_i = \int_V \Theta R_i c_i \, dx.$$  \hspace{1cm} (3)

Typically, $R_i \equiv 1$ and $\Theta \equiv \phi$ in (1) with $\phi$ being the porosity of porous media. Clearly, if $R_i > 1$, the integral in (3) can be split into two parts, the integral of $\Theta c_i$ and the integral of $(R_i - 1)\Theta c_i$. The first one defines the content of contaminant in flowing groundwater in the pores of porous media, while the second one must characterize some form of contaminant that is not transported within the flowing groundwater. In next section we give more details on adsorption processes that can be described using this approach.

Analogously, the function $S_i \in (0,1)$ describes that only a part of the contaminant concentration $S_i c_i < c_i$ is transported within the flowing groundwater, while the rest part $(1 - S_i)c_i$ is considered to be immobile. In next section we give more details on how such approaches can be used to model the precipitation of contaminants.

Finally, $F_i$ stands for all reaction terms and, optionally, some external sources/sinks due to, e.g., wells. Concerning the reaction terms, only some specific types are supported directly in $r^3 t$, see Section 2.2 later for particular examples. Nevertheless each $F_i$ can be enhanced by additional types of reactions by implementing corresponding procedures in C language as it is done, e.g., in [14].

If $c_i$ represents the unknown concentration of so called “complexing agent” [13] then this chemical species undergoes no reaction and one can have $F_i \equiv 0$ in (1). The most important type of reaction that, if present, takes place in all parts of porous media is the decay of radioactive contaminants. It is described by $F_i = G_i$ and

$$G_i = -\Theta R_i \lambda_{ij} c_i + \sum_k \Theta R_k \lambda_{ik} c_k.$$  \hspace{1cm} (4)
Here, the constant $\lambda_{ij}$ describes the reaction rate for the decay of the $i$-th contaminant ("nuclide") to $j$-th contaminant and analogously for $\lambda_{ki}$. Note that several nuclides with concentrations $c_i$ can decay to the $i$-th nuclide.

The system (1) is written in a conservative ("divergent") form that can be derived from mass balance laws for all involved processes of transport and retention, see [13] for details. One can transfer (1) to integral formulation that is the starting point for numerical approximations by finite volume methods. In such a way, the numerical methods will mimic in a discrete form the involved mass balance laws.

It is important to note that (1) must be consistent with the partial differential equation that is fulfilled by $\mathbf{V}$, the "flow equation". We must suppose that the flow regime is not influenced by the presence of contaminants. Considering in (1) a single non-reactive contaminant such that $c_1(t, x) \equiv 1$ with no sources and sinks one obtains
\[
\nabla \cdot \mathbf{V} = 0.
\]
Clearly, when introducing any particular form of the general model (1), one has to define $\Theta$ and $F_i$ in (1) accordingly with (5).

Finally, the equations (1) are completed with some initial conditions $c_i(0, x) = C_i(0, x)$ and boundary conditions of several types including the value-dependent one (Dirichlet) $c_i(t, \gamma) = C_i(t, \gamma)$, $\gamma \in \partial \Omega$ and the flux-dependent ones (e.g., Neumann, Newton, inflow/outflow, transmission, etc.) [13]. In the latter case, the flux $\mathbf{N} \cdot \mathbf{J}_i$ in outward normal direction $\mathbf{N}$ at the boundary $\partial \Omega$ of domain $\Omega$ (or only its diffusion part in the case of so called outflow boundary) is replaced with some given values.

2.2 System of ODEs

Many processes of reactive transport can be modelled by extending the system (1) with additional unknown functions $c_i$, $i = I + 1, \ldots, I$ and with related ordinary differential equations (ODEs) written analogously to (1),
\[
\Theta \partial_t (R_i c_i) = F_i. \tag{6}
\]
Due to a dependence of $F_i$ (and possibly also of $R_i$) on several unknown concentrations, the equations (6) and (1) are coupled.

In $r^3t$ such extension is used to describe another form of presence for each contaminant additionally to its dissolved (and precipitated) form in flowing groundwater. Firstly, each contaminant can be also adsorbed to the surface of pores in porous media. Secondly, each contaminant can occur in a dissolved form in immobile ("dead-end") pores of porous media, where the groundwater is present but not flowing. Finally, the contaminant can be adsorbed also in immobile pores of porous media.

Consequently, we denote the concentration of $i$-th contaminant in flowing (mobile pore) groundwater by $c_i$, the adsorbed concentration in mobile pores by $c_{i+I}$, the immobilized concentration in immobile pore water by $c_{2I+i}$, and the adsorbed concentration in immobile pores by $c_{3I+i}$ with $i = 1, \ldots, I$. The total mass $M_i = M_i(t)$ of contaminant in any volume $V \subset \Omega$ of porous media $\Omega$ is then given by
\[
M_i(t) = \sum_{k=0}^{3} \int_V \Theta^{(k)}(x) c_{kI+i}(t, x) \, dx. \tag{7}
\]
where the factors $\Theta^{(k)}$, $k = 1, \ldots, 3$, define the computation of partial content (mass) of the $i$-th contaminant in, say, the $k$-th part of porous media and $\Theta^{(0)} \equiv \Theta$.

In general, one can define in $r^3t$ his/her own form of factors $\Theta^{(k)}$ by implementing a C language code to describe a specific application of $r^3t$. Nevertheless, the standard usage of $r^3t$ for the modelling of contaminant transport consists of defining several physical parameters in some input text files [13, 22], and the factors $\Theta^{(k)}$ are computed accordingly.

Particularly, if all parts of porous media are considered by the user in the model, then $\Theta = \phi$, $\Theta^{(1)} = (1 - \phi - \phi_{im})(1 - g)\rho_m$, $\Theta^{(2)} = \phi_{im}$, and $\Theta^{(3)} = (1 - \phi - \phi_{im})(1 - g)\rho_m$ where $\phi \in (0, 1)$ is the porosity characterizing the mobile pores part of porous media, $\phi_{im} \in (0, 1 - \phi)$ is the porosity of immobile pores part, $\rho_m$ is the density of solid matrix and $g \in (0, 1)$ is a constant, see also [13] for more details.

Next we describe some particular forms of reactions given by (6) as used in $r^3t$.

The adsorption from mobile pore groundwater is described for $i = I + 1, \ldots, 2I$ by
\[
\Theta^{(1)} \partial_t c_i = \Theta^{(1)} k_i (K_{i-1} + S_{i-1} - c_i) + G_i, \tag{8}
\]
where $G_i$ is defined analogously to (4). The sorption coefficient $K_{i-1}$ is a constant or a function of (several) concentrations, the coefficient $k_i$ describes a constant reaction rate. The presence of coefficient $S_{i-1}$ in (8) expresses the fact that only dissolved contaminant can be adsorbed. The ODEs (8) models the so-called slow (non-equilibrated) sorption case, the case of fast sorption (or in equilibrium) will be described later using appropriate
definition of retardation factors. Note that no retardation is considered in (8).

If also immobile pore groundwater is involved together with adsorption, the following ODEs are included for \( i = 2I + 1, \ldots, 3I \) to model the exchange of contaminants between mobile and immobile pores groundwater,

\[
\Theta^{(2)} \Theta_{\partial_t c_i} = k_i (c_{i-2I+i} - c_i) + G_i,
\]

and the following ones for \( i = 3I + 1, \ldots, 4I \) for the exchange between the dissolved and adsorbed form of contaminant in immobile pores groundwater,

\[
\Theta^{(3)} \Theta_{\partial_t c_i} = \Theta^{(3)} k_i (K_{-I+i} c_{i-1+i} - c_i) + G_i.
\]

Note that no precipitation is considered in \( i^d \) when using (9) and (10).

Of course, the ODEs (8) - (10) are accompanied with some initial conditions to define the values of \( c_i(0, x) \).

Finally, the related processes must be included also to the equations (1) for dissolved concentration in mobile pores groundwater by a corresponding form of \( F_i \) namely \((i = 1, \ldots, I)\)

\[
F_i = G_i - k_{I+i} (K_i S_i c_i - c_{I+i}) - k_{2I+i} (c_i - c_{2I+i}).
\]  

3 Transport of radioactive contaminants with different retardation factors

The most important particular form of (1) is obtained when the transport of several radioactive contaminants with retention due to fast sorption (in equilibrium) is considered. Such situation leads to a system of transport equations with different retardation factors \( R_i > 1 \) in (1) and is studied, analytically or numerically, in several papers [6, 7, 19, 32]. To derive such system, we take first \( R_i = 1 \) in (1) and sum it with (8) to obtain

\[
\Theta \Theta_{\partial_t c_i} + \Theta^{(1)} \Theta_{\partial_t c_{I+i}} + \nabla \cdot \mathbf{J}_i = \Theta \left( \sum_k \lambda_{ki} c_k - \lambda_{ji} c_i \right) + \Theta^{(1)} \left( \sum_k \lambda_{ki} c_{I+k} - \lambda_{ji} c_{I+i} \right).
\]

Furthermore, we consider

\[
c_{I+i} = K_i S_i c_i,
\]

that can be obtained by dividing (8) with \( k_i \) and noting that for fast adsorption process the term with \( 1/k_i \) can be neglected.

Using (13) in (12) we can now introduce the factor \( R_i \) by denoting

\[
R_i = 1 + \frac{\Theta^{(1)}}{\Theta} K_i S_i,
\]

and one obtains the following particular form of (1),

\[
\Theta \Theta_{\partial_t c_i} + \nabla \cdot \mathbf{J}_i + \Theta \lambda_{ji} R_i c_i = \Theta \sum_k \lambda_{ki} R_k c_k.
\]

Note that if \( S_i = 1 \) and \( K_i \) in (13) is at most space dependent, the coefficient \( R_i = R_i(x) > 1 \) can be viewed as a retardation factor, because (15) can be divided by \( R_i \) and the factor \( 1/R_i \) slows down the effective transport of contaminant.

If the system of equations (15) is linear, the equations are coupled only in one direction given by the chain of decay reactions. It means that each equation for a contaminant that is not a product of other decaying contaminant can be solved independently, see the nuclides in the first row in Figure 2. Once such concentrations of the first row are computed and known, all equations for contaminants in the next row can be solved again independently, see the second row of Figure 2.

In general the equations (15) represent a nonlinear and fully coupled system due to two nonlinear features. These are the nonlinear sorption in equilibrium that is represented by \( R_i = R_i(C_c) \) and the case of precipitation with \( S_i = S_i(C_c) \). The both nonlinear features are even more complicated due to the fact that \( C_c \) denotes the concentration of the \( e \)-th "chemical element" of which several nuclides can be present in groundwater [1, 13] and

\[
C_c = \sum_{l} c_l.
\]

The sum in (16) is realized for the indices \( l \) from a subset of the indices of all nuclides belonging to the same chemical element with the index \( e \), see the particular example of Uranium in Figure 3 where three nuclides belong to one chemical element. In such a way, opposite to the linear system, due to the dependence of \( C_c \) on (possibly) several concentrations \( c_l \), the system (1) is fully coupled and all equations shall be solved at once, compare Figure 3 with Figure 2.

Next we describe the form of nonlinearities in details.
Firstly, the precipitation is modelled in (15) by introducing a solubility limit \( L_e \),
\[
S_i(C_e) = \begin{cases} 
1 & C_e \leq L_e \\
\frac{L_e}{C_e} & C_e > L_e 
\end{cases}
\]  
(17)
where \( L_e > 0 \) and the concentration \( C_e \) is given by (16).

Secondly, the nonlinearity \( R_i = R_i(C_e) \) is determined by the type of sorption isotherms defined by coefficient \( K_i = K_i(S_i(C_e)C_e) \) in (8), (10) and (14). The most well-known choices are the Freundlich and Langmuir isotherms or their combination \((a_i, b_i \text{ and } p_i)\) are some non-negative real constants that have to be defined by users of \( r^3t \),
\[
K_i(s) = \frac{a_i s^{p_i}}{1 + b_i}.
\]  
(18)
Note that opposite to linear case when \( K_i \) is constant (so called Henry isotherms), the role of the retardation factor for the transport with nonlinear sorption \([2]\) is here (so called Henry isotherms), the role of the retardation factor for the transport with nonlinear sorption \([2]\) is here
\[
\lambda_i = 1 + \frac{\Theta(3)}{\Theta(2)} K_i.
\]

The user of \( r^3t \) is not restricted to the particular form of (18) as it can be simply changed by implementing another form of \( K_i = K_i(s) \) (and the derivative \( K_i'(s) \) for nonlinear solver) requiring only few lines of C code in \( r^3t \).

The most difficult type of sorption isotherms to deal with are Freundlich isotherms when \( 0 < p_i < 1 \) in (18). Such isotherms involve a degenerate case for zero concentration when \( R_i'(0) = \infty \) and typical features of hyperbolic equations for conservation laws \([29]\) like a formation of sharp fronts even for smooth initial data can be observed in related numerical simulations, see also \([21]\).

We note that if additionally to the transport of dissolved contaminant given by (15) also the immobilisation of contaminant described by (9) is considered, the fast sorption (10) in immobile pores is treated analogously. Consequently, the ODEs (9) are transformed into the form
\[
\Theta^{(2)} \partial_t (R_i c_i) + \Theta^{(2)} \lambda_{ij} R_i c_i c_j = \Theta^{(2)} \sum_k \lambda_{ki} R_k c_k + k_i (c_{-2I+i} - c_i),
\]  
(19)
where
\[
R_i = 1 + \frac{\Theta^{(3)}}{\Theta^{(2)}} K_i.
\]

To make the description of implemented models in \( r^3t \) complete, one shall note that the coefficients \( K_i \) and \( L_i \) can be given as functions of time and space coordinates. This is the case when the transport of non-reacting complexing agents \([13]\) is included in the overall system of (1) and \( K_i \) and \( L_i \) can be defined by users as functions of their concentrations. Similarly, stochastic modelling of sorption \([2]\) can be (and was) used with \( r^3t \) \([13]\).

4 Numerical methods

To solve the general mathematical model (1) numerically, a general purpose finite volume method is developed in \( r^3t \). Using a modular implementation, several specific variants of this method are developed and included in \( r^3t \) to solve efficiently and accurately the most important particular cases of (1) as described in Section 3. Such methods involve an exact computation of decay reactions \([6]\), first order accurate characteristic based computations of advection with formally no restriction on a choice of time steps \([16, 23]\), and a second order accurate computations of advection with a limiter to reduce the accuracy locally to avoid non-physical oscillations in numerical solution \([18, 20, 24]\). All these specific methods for particular terms in general mathematical model (1) are coupled with the discretization of remaining terms in (1) using a simple operator splitting method \([29]\) that is in general only first order accurate in time.

The primary choice of users in \( r^3t \) is the general purpose finite volume method as depicted in Section 4.1 with an option for three different approximations in time as described in Section 4.2 afterwards. If the advective transport dominates strongly to dispersive transport or the decay reactions dominates to other time dependent processes, the users of \( r^3t \) have the choice of advanced numerical methods for these particular cases as described in Section 4.3 and in Section 5.

4.1 Finite volume method

All numerical methods in \( r^3t \) are based on the vertex-centred Finite Volume Method (FVM), where computational cells, the “finite volumes” \( \Omega_j \subset \Omega \), are dual to finite element mesh, and the nodes \( x_j \) of finite elements \( T_e \subset \Omega \) are centres of finite volumes \( \Omega_j, j = 1, \ldots, J \). For a construction of such finite volume mesh see, e.g. \([9, 10, 15, 27, 33]\).

This choice has several advantages. Firstly, all discretization methods are directly based on an integral form of conservation laws for (1). If two numerical integration rules are accepted as a discrete form of the computation for mass and flux, no numerical errors are introduced to the discrete local and global form of the mass balance property for each contaminant. Secondly, the availability of standard finite element interpolation for the primal mesh enables to compute the gradient of the numerical solution very easily.

Practically all discretization methods used in \( r^3t \) can be viewed as a particular implementation of the following general discretization scheme,
\[
\Delta t^n \sum_k |f_{jk}| N_{jk} \cdot J_{jk} + \Delta t^n |\Omega_j| F^n_j = 0,
\]  
(20)
where
\[
\Delta t^n |\Omega_j| F^n_j = \sum_i |\Omega_j| \Theta^{(2)} R_i^{n+1} c_i^{n+1} = |\Omega_j| \Theta^{(2)} R_i^{n} c_i^{n} - \Delta t^n |\Omega_j| F^n_j.
\]
where the index \( s \) in (20) will be defined later depending on the choice of time discretization method. For simplicity when deriving (20) we skipped the index \( i \) for \( c_i \) in (1). The discretization of ODEs from Section 2.2 is analogous to (20) containing, of course, no transport part, i.e. \( \mathbf{J}_{jk} = 0 \).

The nodal values \( c_j^n \approx c(t^n, x_j) \) are known from the previous time step (or from initial conditions). The value \( \Omega_j(\partial_j R_j c_j^n) \) approximates the mass \( M \) from (3) of contaminant contained in \( \Omega_j \) at \( t = t^n \) in discrete form, and analogously for the term on the l.h.s. of (20) at \( t = t^{n+1} \).

The index \( k \) in (20) stands for all neighbours \( \Omega_k \) of \( \Omega_j \) with non-empty measure \( |\Gamma_{jk}| \) of \( \Gamma_{jk} := \partial \Omega_j \cap \partial \Omega_k \), and the terms \( \mathbf{J}_{jk} \) represent the discrete form of fluxes \( \mathbf{J} \) from (2) over \( \Gamma_{jk} \) and will be described in details later (\( \mathbf{N}_{jk} \)) is the unit outward normal vector w.r.t. \( \Gamma_{jk} \). In fact, the boundary segments \( \Gamma_{jk} \) can be furthermore split to two parts in 2D case (or even several in 3D) that we do not emphasize here to simplify the presentation, see [15] for details.

Consequently, the equations (20) represent the discrete form of integral formulation for the mass balance property and, at the same time, the algebraic system of equations for known nodal values \( c_j^{n+1} \approx c(t^{n+1}, x_j) \).

Not yet described approximations of \( \mathbf{J}_{jk} \) and \( \mathbf{F}_j \) in (20) are discussed in the subsequent section noting that some of these approximations are only first order accurate. If some advanced numerical methods for the approximation of advection are chosen in computations with \( r-t \), see Section 5 later, the numerical flux \( \mathbf{J}_{jk} \) involves only dispersion-diffusion part. Similarly, if an operator splitting method is used to solve decay reactions, the values \( \mathbf{F}_j \) are computed in a separate way, see Section 4.3 later.

4.2 Implicit discretization of transport

The main advantages of the vertex-centred FVM is the possibility to use standard finite element interpolation related to the primal mesh [9,10,27]. Using basis functions \( \Psi_k \) that are well-known from finite element methods, one can interpolate the numerical solution \( c^n(x) \), respectively \( (Sc)^n(x) \), using the nodal values \( c_k^n \).

\[
c^n(x) := \sum_k c_k^n \Psi_k(x), \quad (Sc)^n(x) := \sum_k S_k^n c_k^n \Psi_k(x),
\]

where \( k \) runs through indices of corners of element \( T_i \) for which \( x \in T_i \) and the value \( S_k^n \) is computed from \( c_k^n \) using (17). Analogously to (21) the interpolation functions \( c^{n+1}(x) \) and \( (Sc)^{n+1}(x) \) are defined.

Three choices for the definition of fluxes \( \mathbf{F}_j \) in (20) are available in \( r-t \) that correspond to three different (implicit in time) discretization schemes. Note that the terms \( \mathbf{F}_j \) in (20) are treated analogously.

Firstly, the choice \( n + 1 \) for \( \ast \) in (20)

\[
\mathbf{J}_{jk}^{n+1} := \mathbf{V}_{jk} (Sc)^{n+1}(x_{jk}) - \mathbf{D}_{jk} \nabla (Sc)^{n+1}(x_{jk})
\]

leads to the first order accurate scheme in time and represents the backward Euler scheme, where \( x_{jk} \in \Gamma_{jk} \) is the barycentre of \( \Gamma_{jk} \). The coefficients \( \mathbf{V}_{jk} \) and \( \mathbf{D}_{jk} \) are obtained by evaluating \( \mathbf{V} \) and \( \mathbf{D} \) at \( x = x_{jk} \).

Secondly, one can choose \( n + 1/2 \) for \( \ast \) in (20) using

\[
\mathbf{J}_{jk}^{n+1/2} := 0.5\mathbf{J}_{jk}^n + 0.5\mathbf{J}_{jk}^{n+1}
\]

which gives the second order accurate Crank-Nicolson scheme.

The Crank-Nicolson scheme can be viewed formally as a two-step method. In the first step, the intermediate values \( c_j^{n+1/2} \) are computed by solving the following system of discrete equations

\[
|\Omega_j|\partial_j R_j c_j^{n+1/2} = |\Omega_j|\partial_j R_j c_j^n - \frac{\Delta t^n}{2} \sum_k |\Gamma_{jk}| \mathbf{N}_{jk} \cdot \mathbf{j}_{jk}.
\]

The second (final) step is described by the following implicit scheme using the previously computed intermediate values

\[
|\Omega_j|\partial_j R_j c_j^{n+1} + \frac{\Delta t^n}{2} \sum_k |\Gamma_{jk}| \mathbf{N}_{jk} \cdot \mathbf{j}_{jk}^{n+1} = \frac{|\Omega_j|\partial_j R_j c_j^n}{2}
\]

that represents the nonlinear system of algebraic equations to be solved for unknown nodal values \( c_j^{n+1} \).

It is well known that the Crank-Nicolson scheme is unconditionally stable, nevertheless to have no unphysical oscillations in numerical solution, one should restrict the choice of time step due to (24) as known for explicit discretization schemes.

Finally, a two step method BDF (Backward Difference Formula) can be used, see, e.g., [33], that requires for computation of \( c_j^{n+1} \) also the values \( c_j^{n-1} \). Such a scheme modifies the general scheme (20) by replacing, among others, the first term on the r.h.s. of (20) with different approximation and may not be seen as a mass conservactive scheme in general.

Remark 1 The nonlinear system of algebraic equations (25) is solved using some advanced nonlinear solvers available in UG. The linearization is implemented in \( r-t \) using the analytical form of derivatives for all involved nonlinear coefficients with two exceptions.

Firstly, due to the non-existence of \( S'(c_s) \) at \( c_s = L_s \) (see (17), the so called Picard type of linearization is used instead of Newton type [17] which does not use the derivatives of \( S \). Similarly, due to the non-existence of \( K'(0) \) in the case of Freundlich isotherms with \( 0 < p < 1 \), see (18), the derivatives \( K'(s) \) for \( s \in (0, \epsilon) \) are replaced by the constant value \( K'(\epsilon) \). The nontrivial choice of value \( \epsilon \) must be done by the user of \( r-t \) depending on the value \( p \) in (18) and some other factors.

Remark 2 The matrices arising in algebraic system of linear equations (20) have a block based format where
the number of blocks in one row of a matrix is determined by discretization methods. The sparsity inside of blocks depends on a coupling between unknowns of PDEs and ODEs, and the corresponding sparse format have to be constructed on the run of \( r^t \) depending on the choice of physical parameters made by users, see [31] for details. Using an efficient matrix format, very large system of equations can be solved by \( r^t \). A formal test was reported in [25] for an example with 120 components (i.e., \( I = 30 \) in (1) and \( I = 120 \) in (6)) computed on some coarse computational grid.

### 4.3 Discretization of decay reactions

The system of ODEs describing the decay reactions for \( i = 1, \ldots, I \),

\[
\partial_t (R_i c_i(t)) + \lambda_i R_i c_i(t) = \sum_k \lambda_{ki} R_k c_k(t),
\]

(26)
can be solved exactly for constant retardation factors \( R_i \) and \( t \in [t^n, t^{n+1}] \), see, e.g., [6, 26]. For a nonlinear case \( R_i = R_i(c_i) \), one has to solve the system of (26) for \( \tilde{c}_i = R_i c_i \) and afterwards solve the system of nonlinear algebraic equations \( \tilde{c}_i = R_i c_i \) for \( c_i, i = 1, \ldots, I \). Such procedure is implemented in \( r^t \) and available to choose by users of \( r^t \).

To use the exact solution of (26) in the general discretization scheme (20), the so called operator splitting method [17, 29] is applied by a specific definition of the r.h.s. in (20) for \( j = 1, \ldots, J \) such that

\[
E_j^{n+1/2} := \frac{1}{\Delta t} \Theta_j \left( R^{n+1/2}_i c_i(t^{n+1/2}) - R^n_j c^n_j \right),
\]

(27)
where \( c_i, j(t) \) is obtained by solving (26) with initial condition \( c_i(t^n) = c^n_i \approx c_i(t^n, x_j) \). Note that using (27) in (20) can lead to a time splitting error that can deteriorate accuracy in some cases, see the related numerical experiment in Section 6.1.

If \( F = F(t, x) \) represents an externally given source or sink, some standard quadratures can be used, e.g.,

\[
E_j^{n+1/2} := F(t^{n+1/2}, x_j),
\]

(30)
or even exact integration for some simple cases. If \( F \) represents other types of reaction than described by (26), standard time discretization techniques are used, see Section 4.2.

### 5 Explicit discretization of advection

In this section we consider only purely advection transport of contaminant described by

\[
\Theta \partial_t (Rc) + \nabla \cdot (Vc) = 0.
\]

(28)
In realistic settings of contaminant transport in flowing groundwater the diffusion and dispersion are always present, nevertheless the equation (28) can be considered to be a limit case of advection dominated situation for general transport equation (1).

For hyperbolic equations of conservation laws, explicit discretization schemes are preferable. The background of the derivation of such schemes can be given by the so called Godunov’s method that is based on solving (exact, if possible) so called local Riemann problems, see, e.g., [29].

Analogously to (20), the discretization by finite volume methods applied to (28) leads to discrete equations

\[
|\Omega_j| \Theta_j R^n_j c^{n+1}_j = \Delta t^n \sum_k |\Gamma_{jk}| N_{jk} \cdot V_{jk} c^{n+1}_j.
\]

(29)
To define the values \( c^{n+1/2}_j \) in (29), opposite to the approach of Section 4.2, we use explicit in time discretization methods. This means that we define \( c^{n+1/2}_j \) using only the nodal values \( c^n_j \) and \( c^n_{k,j} \) and those at neighbouring grid points to \( x_j \). Consequently, if the retardation factor \( R \) is not concentration dependant, each discrete equation (29) is trivial to solve for the unknown value \( c^{n+1}_j \).

If one supposes that our numerical solution \( c^n(x) \) is a piecewise constant function with respect to the finite volume mesh, one obtains the well-known first order accurate upwind scheme,

\[
c^{n+1/2}_j := \begin{cases} c^n_j, & N_{jk} \cdot V_{jk} > 0, \\ c^n_{k,j}, & N_{jk} \cdot V_{jk} < 0. \end{cases}
\]

(30)
This scheme is valid only if the CFL restriction for the choice of time step \( \Delta t^n \) is fulfilled. This restriction can be defined by the requirement that all local (grid) Courant numbers (if \( R_j \neq R_i(c_i) \))

\[
c^n_j := \frac{\Delta t^n}{|\Omega_j| \Theta_j R^n_j} \sum_k |\Gamma_{jk}| \max\{0, N_{jk} \cdot V_{jk} \}
\]

(31)
are smaller than or equal to one. For structured grid with uniform grid step \( h \), constant velocity vector \( V = (V_1, V_2, V_3) \) and \( \Theta = \omega \), one obtains the well-known form

\[
c^n = \frac{\Delta t^n}{h} \max\{|V|, |V_1|, |V_2|, |V_3| \}.
\]

The most important advantage of the first order scheme is that it produces numerical solutions that fulfill the local discrete minimum and maximum property,

\[
\min_k \{c^n_j, c^n_{k,j}\} \leq c^{n+1}_j \leq \max_k \{c^n_j, c^n_{k,j}\},
\]

(32)
if the property \( \nabla \cdot V = 0 \) is fulfilled in its analogous discrete form,

\[
\sum_k |\Gamma_{jk}| N_{jk} \cdot V_{jk} = 0.
\]

(33)
Note that (33) can be obtained from (20) in a very natural way by evaluating the discrete equations (29) with the trivial exact solution \( c(x, t) \equiv 1 \) analogously to the derivation of (5). For other cases, that means when (33) is not fulfilled, the min-max property (32) needs not to be fulfilled, see the discussion in next section.
In principal, the Courant number restriction like (31) can be avoided when solving advection equation numerically by implementing "characteristics based" discretization methods, see, e.g., [30, 34, 35]. Such a scheme in the context of finite volume methods, the so called "flux-based method of characteristics" [16], was proposed during the development of r3t and is available for users of r3t. The related numerical scheme is realized by extending in (30) the definitions of $c_{jk}^{n+1/2}$ involving not only the values $c_k^n$ and $c_j^n$ and their neighbours, but also the "neighbours of neighbours" and so on, see [16] for details. An analogous method for 2D/3D pore-scaled modelling of transport using network descriptions of pore space was introduced by Kroll et al. [18].

In general, the first order upwind scheme (30) introduces too much numerical (artificial) diffusion that can smear extensively the resulted numerical solution. The remedy is to replace the piecewise constant profile of $c_i^0(x)$ used to derive (30) by some linear profile with which the Godunov method is used [29].

In [18], a very simple extension of (30) to a (formally) second order accurate scheme is described using the definition (31) of Courant number $C_i^n$. The scheme can be written in the form of (29) with

$$c_{jk}^{n+1/2} = \begin{cases} (1 - C_j^0) c_{jk}^n + C_j^0 c_k^n, & N_{kj} \cdot V_{kj} > 0, \\ (1 - C_k^0) c_{jk}^n + C_k^0 c_j^n, & N_{kj} \cdot V_{kj} < 0, \end{cases}$$

where $c_{jk}^n$ has to be computed using some linear interpolation, e.g. $c_{jk}^n = 0.5(c_k^n + c_j^n)$.

The scheme (34) can be viewed as a convex combination of "central" and upwind scheme depending on the local grid Courant number. For one dimensional case it takes the form of so called Lax-Wendroff scheme, see [18, 29]. A slightly modified version of (34) using averaged gradients for each $\Omega_j$ to compute $c_{jk}^n$ in (34) (that is analogous to Fromm's method in 1D [29]) is realized in r3t. Moreover, a limiter procedure in the context of 2D/3D unstructured grid was developed and implemented for r3t, see [18] for a description. The final scheme produces again numerical solutions that fulfill the discrete min-max principle (32) and is extended for arbitrary Courant numbers when it becomes first order accurate [18].

Note that for the nonlinear case $R_j = R_j(c_j)$ one has to apply instead of (31) the following definition of the local grid Courant number (if $c_k^n \neq c_j^n$), see [20],

$$C_i^n := \frac{\Delta t^n}{|\Omega_j|} \sum_k \frac{c_k^n - c_j^n}{R_k^n c_k^n - R_j^n c_j^n} |K_{kj}| \max \{0, N_{kj} \cdot V_{kj}) \}.$$  

A first order accurate Godunov method for purely advective 1D transport with sorption isotherms (18) having a time restriction based on (35) is implemented and available in r3t, see [17,21]. We note that in [21] analytical solutions of Riemann problems used in this Godunov method are described that are valid for large times.

Finally we comment the numerical solution of a coupled system of transport equations

$$\partial_t (R_i c_i) + \nabla \cdot (V c_i) + \lambda_j R_i c_i = \sum_k \lambda_k R_k c_k.$$  

(36)

To solve (36), the operator splitting method is used, see [17,29]. Firstly, only the reaction part of (36) is solved, in fact exactly, see Section 4.3, and afterwards the results are used as the initial conditions for the numerical solution of advection equation (28). If all retardation factors $R_j$ are identical, no time splitting error is introduced, because both operators are commutative, see [29].

If retardation factors $R_j$ in (36) are different, time splitting errors can dominate the global discretization error, especially if large time steps are used. The advantages of the flux-based method of characteristics is that any large time step $\Delta t^n$ can be viewed as the sum of partial ("critical" [16] or "residence" [28]) time steps, and operator splitting can be applied according to them. Although this is far from trivial, it is implemented in r3t and described in [18]. A simple illustrative example to show the advantages of this approach will be presented in section 6.1.

5.1 Advection level set equation

A great advantage of r3t is to offer several choices how the velocity field $V$ in (1), respectively in (28), is defined. Such choices include the possibility of analytical definition for $V = V(x)$ using C language functions or as an interpolation function if the velocity is given only in grid points as a results of some numerical simulation. Another choice is to compute $V$ from the Darcy law [8,12] when some approximation of pressure, permeability, etc., are given.

As a consequence of such great flexibility, the velocity values $V_{jk}$ evaluated in integration points $x_{jk}$ needs not to fulfill exactly the condition (33) that represents the discrete form of $\nabla \cdot V = 0$. In fact, even if some analytical function $V(x)$ fulfills pointwise $\nabla \cdot V(x) = 0$, $x \in \Omega$, it does not mean it fulfills (33). In general, the condition (33) can be expected to be fulfilled if the continuity equation $\nabla \cdot V = 0$ is solved with identical finite volume method and on the same grid as the advection equation (28).

If the mass conservative discretization scheme (29) to solve (28) is used with some velocity field that does not fulfill (33), the numerical solution given by (29) does not fulfill the discrete min-max principle (32). The simplest consequence is that even the trivial solution $c(t,x) \equiv \text{const}$ of (28) is not reproduced by the numerical scheme (29) using (30) or (34).

Such behaviour is illustrated by Fig 4, where the top picture shows numerical velocities obtained by solving $\nabla \cdot V = 0$ using software tools $d^3f$ with the Darcy law for $V$ [12]. To these numerical velocities some post-processing procedures is applied afterwards [12] to make
them smooth and easy to represent, so the conditions (33) is slightly violated. The right picture shows the computation of advection transport using $r^3t$ with constant initial concentration on the same grid as V with $d^3f$.

The exact solution shall remain constant, but this is not the case for the numerical solution given by (29), where an influence of small artificial sources/sinks occurs due to the fact that (33) is not valid.

To avoid such behaviour of numerical solution, one can reformulate the advection equation (28) to the non-divergent form

$$
\Theta \partial_t (Rc) + \mathbf{V} \cdot \nabla c = 0
$$

that is equivalent to (28) if $\nabla \cdot \mathbf{V} = 0$. The advection equation (37) is known from literature as “colour equation” [29] or “level set equation” [23, 24]. In general, it does not prescribe any conservation law for $c$, but another important property that $c$ remains constant along characteristic curves. Consequently, the solution of (37) shall fulfill the min-max principle for arbitrary velocity $\mathbf{V}$ even if $\nabla \cdot \mathbf{V} \neq 0$.

An analogous discretization to the scheme (29) for the transport equation in non-divergent form is derived in [23] that produces numerical solutions fulfilling the discrete min-max principle (32) without assuming (33). The scheme takes the following simple form

$$
|\Theta_j| \Theta_j R_{jk}^{n+1} c_j^{n+1} = |\Theta_j| \Theta_j R_{jk}^n c_j^n - \Delta t^n \sum_k |F_{jk}| N_{jk} \cdot \mathbf{V}_{jk} \left( c_{jk}^{n+1/2} - c_{jk}^{n-1/2} \right).
$$

If only a first order accurate form is considered, $c_j^{n+1/2} := c_j^n$, a second order accurate scheme is given in [24]. Note that if (33) is valid, scheme (38) is equivalent to (29).

The numerical scheme (38) is available in $r^3t$ including its extension for arbitrary large Courant numbers [23] and can be used by users if the advection in (1) is not expressed in divergent form.

6 Numerical experiments

In [16–20] several detailed studies of some examples computed with software tools $r^3t$ can be found. Particularly, an example of a decay chain of four contaminants in groundwater flow with constant velocity is computed in [19] and compared with analytical solution in [7]. In [16] an example of scalar advection-diffusion equation with a rotating Gaussian impulse is computed and compared with analytical solution and with results in [36] where several different numerical methods are used to compute the example, see also [33]. In [18], the example of rotating Gaussian impulse is extended to a decay chain of three contaminants with different retardation factors.

In this paper we present some additional examples to illustrate the typical behaviour of numerical solutions for the most important particular cases of the general mathematical model. We start with a simple example for which several features of the mathematical model and the used numerical methods can be clearly compared. Finally, a brief illustration of complex computations with $r^3t$ are described.

6.1 Illustrative examples

To illustrate a typical behaviour of numerical solution for the most important particular cases of general mathematical model (1), we introduce a simple example of three contaminants ($i = 1, 2, 3$):

$$
\partial_t (R_i c_i) + \partial_x (S_i c_i) - 0.005 \partial_{xx} (S_i c_i) - 0.001 \partial_{yy} (S_i c_i) + R_i \lambda_i c_i = R_{i-1} \lambda_{i-1} c_{i-1},
$$

where $\lambda_0 = 0.0, \lambda_1 = 0.4, \lambda_2 = 0.3, \lambda_3 = 0.2$. Note that the right hand side of (39) for $i = 1$ is set to zero. The initial condition is nonzero only for $c_1$ with a finite support of a circular shape (see Figure 5). The domain is $(0, 2) \times (0, 1)$ and the results are presented for $t = 1$.

In our first numerical experiment, we simulate the linear case described by $R_1 = 1, R_2 = 3, R_3 = 9$ and $S_1 = S_2 = S_3 = 1$ using the flux-based method of characteristics for the advection-reaction part of [18] and the implicit time discretization of diffusion using different grids and time steps, see the results presented in Figure 5.

For this example, the first contaminant is transported dominantly by the advection from left to right with a little influence of longitudinal dispersion. At the same time, it decays to the second contaminant that decays itself to the third one. The second contaminant is transported with three times slower advection speed than the first contaminant due to the retardation described by $R_2$ (and analogously for the third contaminant). Therefore, the second and third concentrations create an elongated profile in $x_1$ direction at $t = 1$ with the front concentration occurring dominantly due to the decay reaction.
Fig. 5 Comparison of computations with structured and unstructured grid and with small and large time steps. The first column presents the initial function for the first contaminant, the initial structured and unstructured grid. The 2nd column presents results for (39) using the structured grid and 32 time steps with the first line showing the concentration of the first contaminant and so on. The 3rd column presents analogous results for the unstructured grid and 143 time steps. The 4th column presents analogous results to the 3rd column, but using only 18 time steps with the flux-based method of characteristics. The colours for contour lines in each row denotes identical values of contaminants, but they differ in columns.

The most precise results can be obtained for a structured grid that is aligned to velocity field. Nevertheless, comparable results can be obtained with an unstructured (unaligned) grid if the discretization step in space is halved when compared to the structured grid computations. Note that in the computations, the initial structured is three times uniformly refined, the nonstructured grid is refined four times.

Moreover, the flux-based method of characteristics with the local time splitting for decay reactions enable to use eight time larger time steps (i.e., the maximal grid Courant number being approximately 8) without deteriorating the accuracy of results too much.

To make a very clear visual comparison between the standard operator splitting [29] and the one with "local time step operator splitting" [18], we compute (39) on the unstructured grid with only two (!) time steps, i.e., $\Delta t = 0.5$, see Figure 6. In the left column one can clearly recognize the two intermediate results of decay reactions for the second and third contaminant that produces very inaccurate and unrealistic numerical results if the standard operator splitting is used with such a large time step. The second column presents analogous numerical results for $\Delta t = 0.5$ using the local time step operator splitting in the flux-based method of characteristics [18].

In our last experiments we illustrate an influence of nonlinear extensions to the simple model (39). Firstly, we change the constant $R_1 = 1$ to $R_1 = R_1(c_1) = (1 + c_1^{p-1})$ with $p = 0.85$ to compute the nonlinear retardation of the transport for the first contaminant due to fast sorption with Freundlich type of isotherm. In Figure 7 one can clearly recognize a sharp front in the concentration profile of the first contaminant caused by the retardation factor $1/R'(c_1)$ that slows down the transport of very small concentrations.

Secondly, we change the example (39) by replacing $S_2$ and $S_3$ with (17) where the solubility limits $L_2$ and $L_3$ are chosen a little bit smaller than the maximal concentrations of the second and third contaminants in the experiment as presented in Figure 5. Consequently, when these limits are reached by the corresponding concentrations (and exceeded due to the product of decay reaction, i.e, $c_2 > L_2$ or $c_3 > L_3$), the precipitation occurs as described in Section 3. As it can be observed in the right column of Figure 7, only the dissolved part of contaminant is transported, therefore a sharp interface is created.
in (small) regions where the overall concentrations \(c_2\) and \(c_3\) cross their solubility limits \(L_i\). Note that this example was solved using fully implicit time discretization \((22)\).

6.2 Example of large scale computations

The software package \(r^3t\) is based on UG toolbox that enables large scale computations on parallel computers. To illustrate this feature, the following test example is presented \([22]\).

The example is solved on a complex 3D domain, see the top picture of Figure 8 where also some coarse grid distributed on 16 processors of parallel computer is given. The computational test domain describes a part of a subsurface with several geological layers. A stationary numerical velocity field was obtained with \(d^3f\) \([12]\) by prescribing some inflow and outflow boundary conditions. Due to different permeabilities, a nontrivial 3D flow regime develops that skips less permeable layers and follows a path from the left bottom part of the domain to the right top part, see Figure 8.

This velocity was saved in a file in \(d^3f\) and read afterwards by \(r^3t\) to realise simulations for transport of two nuclides described by equations \((15)\). A constant source for the first nuclide was prescribed at the inflow boundary for some given time period and set to zero afterwards. Due to decay and different retardation factors, both radionuclides are transported with different speeds. Figure 9 plots an isosurface corresponding to 10\% of maximal concentrations for two different time points. A video of this transient simulation can be found on internet starting at atlas.gesc.uni-frankfurt.de/~pfrolkovic.

7 Conclusions

The following concept is successfully applied in software tools \(r^3t\). Firstly, the mathematical model and finite volume method to solve it numerically are presented in a rather general form not restricted to particular applications of radioactive contaminant transport in flowing groundwater. This feature has enabled recent enhancements of \(r^3t\) for more complex applications like colloidal-bound radionuclide transport \([14]\) or contaminant transport in fractured porous media \([11]\). Secondly, the general purpose finite volume method is implemented in a modular way containing advanced methods for numerical solution of the system of decay reactions and advection dominated transport with general (even non-divergence free) velocity field and different retardation factors for each component. Taking into account that large scale computations can be realised with \(r^3t\) on parallel computers for long time simulations and complex 3D geological domains, one can use \(r^3t\) for a realistic modelling of radioactive contaminant transport in flowing groundwater.
References


