# Mobile and immobile gaseous transport: Embedded analytical solutions to finite volume methods

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**Abstract.** We introduce a solver method for mobile and immobile transport regions. The motivation is driven by deposition processes based on chemical vapor problems.
We analyze the coupled transport-reaction equation with mobile and immobile areas.
We apply analytical methods, such as Laplace-transformation, and for the numerical methods we apply Godunov's scheme, see [17] and [23].
The method is based numerically on flux-based characteristic methods and is an attractive alternative to the classical higher-order TVD methods, see [18]. In this article we will focus on the derivation of the analytical solutions for general and special solutions of the characteristic methods, that are embedded into a finite volume method.
At the end of the article we illustrate the higher-order method for different benchmark problems. Finally the method is proposed with realistic results.

**Key words:** advection-reaction equation, mobile-immobile transport, Godunov's method, Laplace transformation, analytical solutions.
**AMS subject classifications.** 35K15 35K57 47F05 65M60 65N30

## 1 Introduction

We study real-life problems in the direction of deposition processes given by transport and reaction models.

The modeling is based an a homogenization of the underlying media, see [3] and [4].

The equations are coupled with the reaction terms and are presented as follows.

$$\begin{aligned} &\partial_t R_i u_i + \nabla \cdot \mathbf{v}\ u_i = -\lambda_i\ R_i\ u_i + \lambda_{i-1}\ R_{i-1}\ u_{i-1} \\ &+\beta(-u_i + g_i) \ \text{ in } \Omega \times (0,T)\ , \end{aligned} \tag{1}$$

$$u_{i,0}(x) = u_i(x,0) \text{ on } \Omega \,, \tag{2}$$
$$\partial_t R_i g_i = -\lambda_i \, R_i \, g_i + \lambda_{i-1} \, R_{i-1} \, g_{i-1} \tag{3}$$
$$+\beta(-g_i + u_i) \text{ in } \Omega \times (0,T) \,,$$
$$g_{i,0}(x) = g_i(x,0) \text{ on } \Omega \,, \tag{4}$$
$$i = 1, \ldots, m \,,$$

where $m$ is the number of equations and $i$ is the index of each component. The unknown mobile concentrations $u_i = u_i(x,t)$ are considered in $\Omega \times (0,T) \subset I\!R^n \times I\!R^+$, where $n$ is the spatial dimension. The unknown immobile concentrations $g_i = g_i(x,t)$ are considered in $\Omega \times (0,T) \subset I\!R^n \times I\!R^+$, where $n$ is the spatial dimension. The retardation factors $R_i$ are constant and $R_i \geq 0$. The kinetic part is given by the factors $\lambda_i$. They are constant and $\lambda_i \geq 0$. For the initialization of the kinetic part, we set $\lambda_0 = 0$. The kinetic part is linear and irreversible, so the successors have only one predecessor. The initial conditions are given for each component $i$ as constants or linear impulses. For the boundary conditions we have trivial inflow and outflow conditions with $u_i = 0$ at the inflow boundary. The transport part is given by the velocity $\mathbf{v} \in I\!R^n$ and is piecewise constant, see [13] and [14]. The exchange between the mobile and immobile part is given by $\beta$.

The paper is organized as follows. One of the main contributions are the one-dimensional analytical solutions. The application for reaction equations are described in section 2. In section 3, the construction of the analytical solutions for the convection reaction equations in different situations is presented. The discretization method, based on embedded analytical solutions to finite volume schemes is discussed in section 4. The verification of the new discretization method in various numerical examples is performed in section 5. At the end of this paper we introduce future works.

## 2 Analytical solutions for reaction equation

In the next section we deal with the following system with piecewise constant velocities for the coupled transport in one dimension. The equation is given as

$$R_i \partial_t u_i = -R_i \lambda_i u_i + R_{i-1} \lambda_{i-1} u_{i-1} \,, \tag{5}$$

for $i = 1, \ldots, m$, whereas $m$ denotes the number of equations. The unknowns $u_i = u_i(x,t)$ denote the contaminant concentrations. They are reacting with constant rates $\lambda_i$ and $R_i$ are the retardation factors.

We assume a irreversible form of a decay chain, e.g. $\lambda_0 = 0$, and for each contaminant given single source terms $\lambda_{i-1} u_{i-1}$.

The analytical solutions for equal retardation factors can be found in [31]. We enlarge the solutions for different retardation factors and special initial conditions.

$$c_1(t) \; = c_{01} \exp(-\lambda_1 t), \tag{6}$$

$$c_i(t) = c_{0i}\exp(-\lambda_i t) + \sum_{m=1}^{i-1} c_{0m}\frac{R_m}{R_i}\Big(\prod_{j=m}^{i-1}\lambda_j\Big)\sum_{m=1}^{i}\frac{\exp(-\lambda_j t)}{\prod_{k=m,k\neq j}^{i}(\lambda_k-\lambda_j)} \tag{7}$$

where $c(0) = (c_{01}, \ldots, c_{0i})^t$ are the initial condition. We assume $i$ components.

**Definition 1.** *We define for the products and summations:*
*1.)* $\prod_{j=m}^{i} a_j = 1$ *for* $m = 1, i = 0$,
*otherwise we use the notation.*
*2.)* $\sum_{j=m}^{i} a_j = 0$ *for* $m = 1, i = 0$,
*otherwise we use the notation.*

*Remark 1.* For reversible reaction processes, there exists also analytical solutions, see [7]. For such solutions, we have to solve a coupled linear equation system.

## 3 Analytical solutions for convection-reaction equation

In the following we construct the solutions for the convection-reaction equations in different initial conditions and coupled situations.

### 3.1 Piecewise-constant and piecewise-linear initial conditions

In the next section we deal with the following system with piecewise constant velocities for coupled transport in one dimension. The equation is given as

$$\partial_t u_i + v_i \partial_x u_i = -\lambda_i u_i + \lambda_{i-1} u_{i-1} \,, \tag{8}$$

for $i = 1, \ldots, m$, whereas $m$ denotes the number of equations. The unknowns $u_i = u_i(x,t)$ denote the contaminant concentrations. They are transported with constant (and in general different) velocities $v_i$ and decay with constant reaction rates $\lambda_i$. The spatiotemporal domain is given by $(0,\infty)\times(0,T)$.

We assume a simple (irreversible) form of a decay chain, e.g. $\lambda_0 = 0$, and for each contaminant given single source terms $\lambda_{i-1}u_{i-1}$. For simplification, we assume that $v_i > 0$ for $i = 1, \ldots, m$. The case $v_i < 0$ can be treated analogously. Owing to (8), all velocities $v_i$ must have the same sign and must be piecewise constant for the cell $i$. Furthermore we do not allow piecewise equal parameters for the case $v_i = v_{i-1}$ and $\lambda_i = \lambda_{i-1}$, for $i = 2, \ldots, m$ . In special solutions we will allow these cases.

The analytical solutions for equal retardation factors can be found in [31]. We enlarge the solutions for different retardation factors and special initial conditions.

We will derive the analytical solutions with piecewise linear initial conditions, but all other piecewise polynomial functions could be derived as shown in the following.

For the boundary conditions we use zero concentrations at the inflow boundary $x = 0$. The initial conditions are defined for $x \in (0, 1)$,

$$\begin{aligned} u_1(x,0) &= \begin{cases} ax + b \,, & x \in (0,1) \\ 0 \qquad , \text{otherwise} \end{cases} \,, \\ u_i(x,0) &= 0 \,, \quad i = 2, \ldots, m \,, \end{aligned} \tag{9}$$

where $a$ and $b$ are arbitrary constants.

We use the Laplace transformation for the translation of the partial differential equation to the ordinary differential equation. The transformations for this case are given in [6], [16] and [19].

In equation (8) we apply the Laplace transformation given in [1] and [5]. For that we need to define the transformed function $\hat{u} = \hat{u}(s,t)$:

$$\hat{u}_i(s,t) := \int_0^\infty u_i(x,t)\, e^{-sx}\, dx \,. \tag{10}$$

From (8), the functions $\hat{u}_i$ satisfy the transformed equations

$$\partial_t \hat{u}_1 = -\left(\lambda_1 + s v_1\right) \hat{u}_1 \,, \tag{11}$$

$$\partial_t \hat{u}_i = -\left(\lambda_i + s v_i\right) \hat{u}_i + \lambda_{i-1} \hat{u}_{i-1} \,, \tag{12}$$

and the transformed initial conditions for $s \in (0, \infty)$,

$$\hat{u}_1(s,0) = \left(\frac{a}{s^2} + \frac{b}{s}\right)\left(1 - e^{-s}\right) + \frac{a}{s}\, e^{-s} \,, \tag{13}$$

$$\hat{u}_i(s,0) = 0 \,, \quad i = 2, \ldots, m \,. \tag{14}$$

We denote for further solutions:

$$\Lambda_i = \prod_{j=1}^{i-1} \lambda_j \,. \tag{15}$$

The equation (12) is solved with the solution methods for the ordinary differential equation, described in [16], and the more general case is presented in [6].

Thus we find the exact solution of (11) and (12):

$$\hat{u}_1 = \hat{u}_1(s,0)\, e^{-(\lambda_1 + s v_1)\, t} \,, \tag{16}$$

for $i = 2, \ldots, m$ ,

$$\hat{u}_i = \hat{u}_1(s,0)\; \Lambda_i \sum_{j=1}^{i} e^{-(\lambda_j + s v_j) t} \prod_{\substack{k=1 \\ k \neq j}}^{i} \left(s(v_k - v_j) + \lambda_k - \lambda_j\right)^{-1} \,. \tag{17}$$

The analytical solution in (17) can have a singular point for a single value of $s$. Nevertheless, this causes no difficulties when we apply the inverse Laplace transformation and thus we do not need to discuss this issue any further.

To obtain the exact solution of (8), we must apply the inverse Laplace transformation on (11). For that we have to apply some algebraic manipulations.

For the first case, let us assume that $v_j \neq v_k$ and $\lambda_j \neq \lambda_k$ for $j \neq k$ and $\forall j, k = 1, \ldots, m$. Then we can denote

$$\lambda_{kj} = \lambda_{jk} := \frac{\lambda_j - \lambda_k}{v_j - v_k} \,. \tag{18}$$

Furthermore, for the next transformation, we require that the values $\lambda_{jk}$ are different for each pair of indices $j$ and $k$.

The factors $\Lambda_{j,i}$ with $\lambda_j \neq \lambda_k$ for $j \neq k$ and the factor $\Lambda_{jk,i}$ with $\lambda_{jk} \neq \lambda_{jl}$ for $k \neq l$ are given by

$$\Lambda_{j,i} = \left( \prod_{\substack{k=1 \\ k \neq j}}^{i} \frac{1}{\lambda_k - \lambda_j} \right) \,, \quad \Lambda_{jk,i} = \left( \prod_{\substack{l=1 \\ l \neq j \\ l \neq k}}^{i} \frac{\lambda_{jl}}{\lambda_{jl} - \lambda_{jk}} \right) \,, \tag{19}$$

where we have the following assumptions:

$$1.\ v_j \neq v_k \ \ \forall j, k = 1, \ldots, m, \text{ for } j \neq k \,, \tag{20}$$

$$2.\ \lambda_j \neq \lambda_k \ \ \forall j, k = 1, \ldots, m, \text{ for } j \neq k \,, \tag{21}$$

$$3.\ \lambda_{jk} \neq \lambda_{jl} \ \ \forall j, k, l = 1, \ldots, m, \text{ for } j \neq k \ \wedge j \neq l \wedge k \neq l, \tag{22}$$

$$4.\ v_j \neq v_k \text{ and } \lambda_j \neq \lambda_k \ \ \forall j, k = 1, \ldots, m, \text{ for } j \neq k \,. \tag{23}$$

From (19), the last term in (17) for a given index $j$ can be rewritten in the following form,

$$\prod_{\substack{k=1 \\ k \neq j}}^{i} \left( s(v_k - v_j) + \lambda_k - \lambda_j \right)^{-1} = \Lambda_{j,i} \sum_{\substack{k=1 \\ k \neq j}}^{i} \frac{\lambda_{jk}}{s + \lambda_{jk}} \Lambda_{jk,i} \,. \tag{24}$$

From (13), adopted in (16) and (17), the standard inverse Laplace transformation can be used and the solution $u_i$ for (8) is given by

$$u_1(x,t) = \exp(-\lambda_1 t) \begin{cases} 0 & , 0 \leq x < v_1 t \\ a(x - v_1 t) + b & , v_1 t \leq x < v_1 t + 1 \\ 0 & , v_1 t + 1 \leq x \end{cases} \,, \tag{25}$$

$$u_i(x,t) = \Lambda_i \left( \sum_{j=1}^{i} \exp(-\lambda_j t) \Lambda_{j,i} \sum_{\substack{k=1 \\ k \neq j}}^{i} \Lambda_{jk,i} A_{jk} \right) \,, \tag{26}$$

$$A_{jk} = \begin{cases} 0 & , 0 \le x < v_j t \\ a(x - v_j t) & \\ +(b - \frac{a}{\lambda_{jk}})(1 - \exp(-\lambda_{jk}(x - v_j t))) & , v_j t \le x < v_j t + 1 \\ (b - \frac{a}{\lambda_{jk}} + a)\exp(-\lambda_{jk}(x - v_j t - 1)) & \\ -(b - \frac{a}{\lambda_{jk}})\exp(-\lambda_{jk}(x - v_j t)) & , v_j t + 1 \le x \end{cases} . \quad (27)$$

Often the critical solutions are to delicate to compute, while influences of the exp-functions are problematic in the higher-order accuracy. Here we propose two methods:

1.) Decay Chains with decay length till six:

$$u_1(x,t) = \exp(-\lambda_1 t) \begin{cases} 0 & , 0 \le x < v_1 t \\ a(x - v_1 t) + b & , v_1 t \le x < v_1 t + 1 \\ 0 & , v_1 t + 1 \le x \end{cases} , \quad (28)$$

$$u_i(x,t) = \Lambda_i \left( \sum_{j=i-6}^{i} \exp(-\lambda_j t) \Lambda_{j,i} \sum_{\substack{k=i-6 \\ k \ne j}}^{i} \Lambda_{jk,i} A_{jk} \right) , \quad (29)$$

$$A_{jk} = \begin{cases} 0 & , 0 \le x < v_j t \\ a(x - v_j t) & \\ +(b - \frac{a}{\lambda_{jk}})(1 - \exp(-\lambda_{jk}(x - v_j t))) & , v_j t \le x < v_j t + 1 \\ (b - \frac{a}{\lambda_{jk}} + a)\exp(-\lambda_{jk}(x - v_j t - 1)) & \\ -(b - \frac{a}{\lambda_{jk}})\exp(-\lambda_{jk}(x - v_j t)) & , v_j t + 1 \le x \end{cases} . \quad (30)$$

2.) Improved Decay Chains with decay length till five and with explicit skipped components :

Often the first component is very dominant and one could not skip this component, so one skip the less dominant components instead.

Here we propose a selective idea to skip the non-dominant chain members, if an acceleration is necessary.

$$u_1(x,t) = \exp(-\lambda_1 t) \begin{cases} 0 & , 0 \le x < v_1 t \\ a(x - v_1 t) + b & , v_1 t \le x < v_1 t + 1 \\ 0 & , v_1 t + 1 \le x \end{cases} , \quad (31)$$

$$u_i(x,t) = \Lambda_i \left( \sum_{j=1, j \notin I}^{i} \exp(-\lambda_j t) \Lambda_{j,i} \sum_{\substack{k=1, k \notin I \\ k \ne j}}^{i} \Lambda_{jk,i} A_{jk} \right) , \quad (32)$$

$$A_{jk} = \begin{cases} 0 & , 0 \le x < v_j t \\ a(x - v_j t) & \\ +(b - \frac{a}{\lambda_{jk}})(1 - \exp(-\lambda_{jk}(x - v_j t))) & , v_j t \le x < v_j t + 1 \\ (b - \frac{a}{\lambda_{jk}} + a)\exp(-\lambda_{jk}(x - v_j t - 1)) & \\ -(b - \frac{a}{\lambda_{jk}})\exp(-\lambda_{jk}(x - v_j t)) & , v_j t + 1 \le x \end{cases} . \quad (33)$$

where $I$ is the set of the non-dominant chain members, e.g. $I = \{2, 3, 6\}$ etc.

3.) Optimized solution with respect to the denominator problem:

Because of the numerical computation for the analytical solution we have derived an improved notation for the equations (25)-(27) and therefore avoid numerical instabilities.

The improved solutions, cf. [13], with the new notation are given as

$$u_i(x,t) = \Lambda_i \sum_{j=1}^{i} \left( L_{j,i} + \sum_{k>j}^{i} \begin{cases} M_{jk,i} & , v_j < v_k \\ M_{kj,i} & , v_k < v_j \\ 0 & , \text{otherwise} \end{cases} \right) , \quad (34)$$
$$\text{with} \quad i = 2, \ldots, m ,$$

where the factors $L_{j,i}$ and $M_{jk,i}$ are defined as:

$$L_{j,i} := \begin{cases} \exp(-\lambda_j t)\ \Lambda_{j,i} \left( a(x - v_j t) + b \right. & \\ \left. -a \sum_{\substack{k=1 \\ k \ne j}}^{i} \frac{1}{\lambda_{jk}} \right) & , v_j t \le x \le v_j t + 1 \\ 0 & , \text{otherwise} \end{cases} , \quad (35)$$

$$M_{jk,i} := \begin{cases} \Lambda_{j,i}\ \Lambda_{jk,i}\ g_{jk} & , v_j t \le x \le v_k t \\ \Lambda_{j,i}\ \Lambda_{jk,i}\ h_{jk} & , v_j t + 1 \le x \le v_k t + 1 \\ 0 & , \text{otherwise} \end{cases} , \quad (36)$$

and the factors $g_{jk}$ and $h_{jk}$ are given as

$$g_{jk} := -(b - \frac{a}{\lambda_{jk}})\exp(-\lambda_j t)\exp(-\lambda_{jk}(x - v_j t)) , \quad (37)$$

$$h_{jk} := (b - \frac{a}{\lambda_{jk}} + a)\exp(-\lambda_j t)\exp(-\lambda_{jk}(x - v_j t - 1)) . \quad (38)$$

*Remark 2.* The analytical solutions of (8) of large components is often very delicate and require plenty of exp-functions. Therefore simplifications can be done with respect to dominant components in the decay chain and improved notations to avoid numerical instabilities. In numerical examples, one can verify that 5-6 successor components will be enough accurate to obtain machine precision results.

### 3.2 Piecewise linear components with all initial conditions

We deal with the following system with piecewise constant velocities for the coupled transport in one dimension. The equation is given as

$$\partial_t u_i + v_i \partial_x u_i = -\lambda_i u_i + \lambda_{i-1} u_{i-1} \,, \tag{39}$$

for $i = 1, \ldots, m$, whereas $m$ denotes the number of equations. The unknowns $u_i = u_i(x,t)$ denote the contaminant concentrations. They are transported with constant (and in general different) velocities $v_i$ and decay with constant reaction rates $\lambda_i$. The spatiotemporal domain is given by $(0,\infty) \times (0,T)$.

We assume a simple (irreversible) form of a decay chain, e.g. $\lambda_0 = 0$, and for each contaminant given single source terms $\lambda_{i-1} u_{i-1}$. For simplification, we assume that $v_i > 0$ for $i = 1, \ldots, m$. The case $v_i < 0$ can be treated analogously. Owing to (39), all velocities $v_i$ must have the same sign and must be piecewise constant for the cell $i$. Furthermore we do not allow piecewise equal parameters for the case $v_i = v_{i-1}$ and $\lambda_i = \lambda_{i-1}$, for $i = 2, \ldots, m$ . In special solutions we will allow these cases.

The analytical solutions for equal retardation factors can be found in [31]. We enlarge the solutions for different retardation factors and special initial conditions.

We will derive the analytical solutions with piecewise linear initial conditions, but all other piecewise polynomial functions could be derived as shown in the following.

For the boundary conditions we use zero concentrations at the inflow boundary $x = 0$. The initial conditions are defined for $x \in (0,1)$,

$$u_p(x,0) = \begin{cases} b_p x + c_p \,, & x \in (0,1) \\ 0 & \text{, otherwise} \end{cases} \quad p = 1, \ldots, m \,, \tag{40}$$

where $b_p$ and $c_p$ are arbitrary constants for $p = 1, \ldots, m$.

We use the Laplace transformation for the translation of the partial differential equation to the ordinary differential equation. The transformations for this cases are given in [6], [16] and [19].

In equation (39) we apply the Laplace transformation given in [1] and [5]. For that we need to define the transformed function $\hat{u} = \hat{u}(s,t)$:

$$\hat{u}_p(s,t) := \int_0^\infty u_p(x,t)\, e^{-sx}\, dx \,. \tag{41}$$

From (39), the functions $\hat{u}_i$ satisfy the transformed equations

$$\partial_t \hat{u}_1 = -\left(\lambda_1 + s v_1\right) \hat{u}_1 \,, \tag{42}$$

$$\partial_t \hat{u}_i = -\left(\lambda_i + s v_i\right) \hat{u}_i + \lambda_{i-1} \hat{u}_{i-1} \,, \tag{43}$$

$$i = 1, \ldots, m \,,$$

and the transformed initial conditions for $s \in (0, \infty)$,

$$\hat{u}_p(s,0) = \left(\frac{b_p}{s^2} + \frac{c_p}{s}\right)(1 - e^{-s}) + (\frac{b_p}{s})\, e^{-s}\,, \quad p = 1, \ldots, m\,. \tag{44}$$

We denote for further solutions:

$$\Lambda_{i,p} = \prod_{j=p}^{i-1} \lambda_j\,. \tag{45}$$

The equations (42) and (43) are solved with the solution methods for the ordinary differential equation, described in [16], and the more general case is presented in [6].

Thus we find the exact solution of (42) and (43):

$$\hat{u}_1 = \hat{u}_1(s,0)e^{-(\lambda_1 + s v_1)t}, \tag{46}$$

$$\hat{u}_i = \hat{u}_i(s,0)e^{-(\lambda_i + s v_i)t} + \sum_{p=1}^{i-1} \hat{u}_p(s,0)\ \Lambda_{i,p}\ \sum_{j=p}^{i} e^{-(\lambda_j + s v_j)t} \prod_{\substack{k=p \\ k \neq j}}^{i} (s(v_k - v_j) + \lambda_k - \lambda_j)^{-1} \tag{47}$$

for $i = 2, \ldots, m$,

The analytical solution in (46)-(47) can have a singular point for a single value of $s$. Nevertheless, this causes no difficulties when we apply the inverse Laplace transformation and thus we do not need to discuss this issue any further.

To obtain the exact solution of (42) and (43), we must apply the inverse Laplace transformation. For that we have to apply some algebraic manipulations.

For the first case, let us assume that $v_j \neq v_k$ and $\lambda_j \neq \lambda_k$ for $j \neq k$ and $\forall j, k = 1, \ldots, m$. Then we can denote

$$\lambda_{kj} = \lambda_{jk} := \frac{\lambda_j - \lambda_k}{v_j - v_k}\,. \tag{48}$$

Furthermore, for the next transformation, we require that the values $\lambda_{jk}$ are different for each pair of indices $j$ and $k$.

The factors $\Lambda_{j,i}$ with $\lambda_j \neq \lambda_k$ for $j \neq k$ and the factor $\Lambda_{jk,i}$ with $\lambda_{jk} \neq \lambda_{jl}$ for $k \neq l$ are given by

$$\Lambda_{j,i,p} = \left(\prod_{\substack{k=p \\ k \neq j}}^{i} \frac{1}{\lambda_k - \lambda_j}\right)\,, \quad \Lambda_{jk,i,p} = \left(\prod_{\substack{l=p \\ l \neq j \\ l \neq k}}^{i} \frac{\lambda_{jl}}{\lambda_{jl} - \lambda_{jk}}\right)\,, \tag{49}$$

where we have the following assumptions:

$$1.\ v_j \neq v_k \ \ \forall j, k = 1, \ldots, m, \text{ for } j \neq k\,, \tag{50}$$

$$2.\ \lambda_j \neq \lambda_k \ \ \forall j,k = 1,\ldots,m, \text{ for } j \neq k\ , \tag{51}$$

$$3.\ \lambda_{jk} \neq \lambda_{jl} \ \ \forall j,k,l = 1,\ldots,m, \text{ for } j \neq k \ \wedge j \neq l \wedge k \neq l, \tag{52}$$

$$4.\ v_j \neq v_k \text{ and } \lambda_j \neq \lambda_k \ \ \forall j,k = 1,\ldots,m, \text{ for } j \neq k\ . \tag{53}$$

From (49), the last term in (46) and (47) for a given index $j$ can be rewritten in the following form,

$$\prod_{\substack{k=p\\k\neq j}}^{i} \left(s(v_k - v_j) + \lambda_k - \lambda_j\right)^{-1} = \Lambda_{j,i,p} \sum_{\substack{k=p\\k\neq j}}^{i} \frac{\lambda_{jk}}{s+\lambda_{jk}} \Lambda_{jk,i,p}\,. \tag{54}$$

From (44) adopted in (46) and (47), the standard inverse Laplace transformation can be used and the solution $u_i$ for (39) is given by

$$u_1(x,t) = \exp(-\lambda_1 t) \begin{cases} 0 & , 0 \leq x < v_1 t \\ a_1(x - v_1 t) + b_1 & , v_1 t \leq x < v_1 t + 1 \\ 0 & , v_1 t + 1 \leq x \end{cases}\ , \tag{55}$$

$$u_i(x,t) = \exp(-\lambda_i t) \begin{cases} 0 & , 0 \leq x < v_1 t \\ a_i(x - v_i t) + b_i & , v_i t \leq x < v_i t + 1 \\ 0 & , v_i t + 1 \leq x \end{cases}\ ,$$

$$= \sum_{p=1}^{i-1} \Lambda_{i,p} \left( \sum_{j=p}^{i} \exp(-\lambda_j t) \Lambda_{j,i,p} \sum_{\substack{k=p\\k\neq j}}^{i} \Lambda_{jk,i,p} A_{jk,p} \right)\ , \tag{56}$$

$$A_{jk,p} = \begin{cases} 0 & , 0 \leq x < v_j t \\ b_p(x - v_j t) & \\ +(c_p - \frac{b_p}{\lambda_{jk}})(1 - \exp(-\lambda_{jk}(x - v_j t))) & , v_j t \leq x < v_j t + 1 \\ (c_p - \frac{b_p}{\lambda_{jk}} + b_p)\exp(-\lambda_{jk}(x - v_j t - 1)) & \\ -(c_p - \frac{b_p}{\lambda_{jk}})\exp(-\lambda_{jk}(x - v_j t)) & , v_j t + 1 \leq x \end{cases}, \tag{57}$$

with $i = 2,\ldots,m$.

Optimized solution with respect to the denominator problem:

Because of the numerical computation for the analytical solution we have derived an improved notation, cf. [13]. The analytical solutions with the new notation are given as:

$$u_1(x,t) = \exp(-\lambda_1 t) \begin{cases} 0 & , 0 \leq x < v_1 t \\ a_1(x - v_1 t) + b_1 & , v_1 t \leq x < v_1 t + 1 \\ 0 & , v_1 t + 1 \leq x \end{cases}\ , \tag{58}$$

$$u_i(x,t) = \exp(-\lambda_i t) \begin{cases} 0 & , 0 \leq x < v_1 t \\ a_i(x - v_i t) + b_i & , v_i t \leq x < v_i t + 1 \\ 0 & , v_i t + 1 \leq x \end{cases}\ ,$$

$$+\sum_{p=1}^{i-1} \Lambda_{i,p} \sum_{j=p}^{i} \left( L_{j,i,p} + \sum_{k>j}^{i} \begin{cases} M_{jk,i,p} \ , v_j < v_k \\ M_{kj,i,p} \ , v_k < v_j \\ 0 \qquad , \text{otherwise} \end{cases} \right) , \tag{59}$$
$$\text{with} \quad i = 2, \ldots, m \ ,$$

where the factors $L_{j,i,p}$ and $M_{jk,i,p}$ are defined as:

$$L_{j,i,p} := \begin{cases} \exp(-\lambda_j t) \ \Lambda_{j,i,p} \left( b_p(x - v_j t) + c_p \right. \\ \left. - \sum_{\substack{k=p \\ k \neq j}}^{i} \frac{1}{\lambda_{jk}} \frac{b_p}{\lambda_{jk}} \right) & , v_j t \leq x \leq v_j t + 1 \\ 0 & , \text{otherwise} \end{cases} , \tag{60}$$

$$M_{jk,i,p} := \begin{cases} \Lambda_{j,i,p} \ \Lambda_{jk,i,p} \ g_{jk,p} \ , v_j t \leq x \leq v_k t \\ \Lambda_{j,i,p} \ \Lambda_{jk,i,p} \ h_{jk,p} \ , v_j t + 1 \leq x \leq v_k t + 1 \\ 0 \qquad\qquad\qquad , \text{otherwise} \end{cases} , \tag{61}$$

and the factors $g_{jk,p}$ and $h_{jk,p}$ are given as

$$g_{jk,p} := -(c_p - \frac{b_p}{\lambda_{jk}}) \exp(-\lambda_j t) \exp(-\lambda_{jk}(x - v_j t - 1)) \ , \tag{62}$$

$$h_{jk,p} := (c_p - \frac{b_p}{\lambda_{jk}} + b_p) \exp(-\lambda_j t) \exp(-\lambda_{jk}(x - v_j t)) \ . \tag{63}$$

*Remark 3.* The analytical solutions of (39) with their initial conditions (40) are used to design discretization methods with embedded analytical support functions, see ideas in [17] and [32]. For more efficient computations, simplifications can be done with respect to dominant components in the decay chain and improved notations to avoid numerical instabilities.

In the next section we derive the analytical solution for general initial conditions.

### 3.3 General initial conditions for piecewise linear convection-reaction equations

To generalize our initial conditions we combine the subsection 3.1 and 3.2.

The equation is given as

$$R_i \partial_t u_i + v_i \partial_x u_i = -R_i \lambda_i u_i + R_{i-1} \lambda_{i-1} u_{i-1} \ , \tag{64}$$

for $i = 1, \ldots, m$, whereas $m$ denotes the number of equations. The unknowns $u_i = u_i(x, t)$ denote the contaminant concentrations. They are transported with constant (and, in general, different) velocities $v_i$ and decay with constant reaction rates $\lambda_i$. The spatiotemporal domain is given by $(0, \infty) \times (0, T)$. Further, $R_i$ is the retardation factor that respects the acceleration or restriction of the time scales.

We have the same assumptions as in the previous sections.

For the boundary conditions we use zero concentrations at the inflow boundary $x = 0$. The initial conditions are defined for $x \in (0, 1)$,

$$u_p(x,0) = \begin{cases} \sum_{q=1}^{Q} b_{p,q}x + c_{p,q} \ , \ x \in [x_q, x_{q+1}] \\ 0 \qquad\qquad\qquad , \qquad \text{otherwise} \end{cases} \tag{65}$$

$$p = 1, \ldots, m \ , \tag{66}$$

where $b_{p,q}$ and $c_{p,q}$ are arbitrary constants of the piecewise quadratic function and $[x_q, x_{q+1}]$ is the interval of the function, $Q$ is the number of intervals.

We use the Laplace transformation for the translation of the partial differential equation to the ordinary differential equation. The transformations for this case are given in [6], [16] and [19].

In equation (64) we apply the Laplace transformation given in [1] and [5]. For that we need to define the transformed function $\hat{u} = \hat{u}(s,t)$:

$$\hat{u}_i(s,t) := \int_0^\infty u_i(x,t)\, e^{-sx}\, dx \, . \tag{67}$$

From (64), the functions $\hat{u}_i$ satisfy the transformed equations

$$\partial_t \hat{u}_1 = -\left(\lambda_1 + sv_1\right) \hat{u}_1 \ , \tag{68}$$

$$\partial_t \hat{u}_i = -\left(\lambda_i + sv_i\right) \hat{u}_i + \lambda_{i-1}\hat{u}_{i-1} \ , \tag{69}$$

and the transformed initial conditions for $s \in (0, \infty)$,

$$\hat{u}_p(s,0) = \sum_{q=1}^{Q} \Big( \left( \frac{b_{p,q}}{s^2} + \frac{c_{p,q}}{s} \right) (1 - e^{-s}) \Big) \tag{70}$$

$$+ \big( \frac{b_{p,q}}{s} \big)\, e^{-s} \big) \, ,$$

$$p = 1, \ldots, m \, . \tag{71}$$

We denote for further solutions:

$$\Lambda_{i,p} = \prod_{j=p}^{i-1} \lambda_j \, . \tag{72}$$

Equation (68)-(69) is solved with the solution methods for the ordinary differential equation, described in [16], and the more general case is presented in [6].

Thus we find the exact solution of (68)-(69):

$$\hat{u}_1 = \hat{u}_1(s,0) \exp(-(\lambda_1 + sv_1)t), \tag{73}$$

$$\hat{u}_i = \hat{u}_i(s,0) \exp(-(\lambda_i + sv_i)t)$$

$$+ \sum_{p=1}^{i-1} \hat{u}_p(s,0)\ \Lambda_{i,p} \ \sum_{j=p}^{i} e^{-(\lambda_j + sv_j)t} \prod_{\substack{k=p \\ k \neq j}}^{i} \left(s(v_k - v_j) + \lambda_k - \lambda_j\right)^{-1} \ , \tag{74}$$

for $i = 1, \ldots, m$.

The analytical solution in (73)-(74) can have a singular point for a single value of $s$. Nevertheless, this causes no difficulties when we apply the inverse Laplace transformation and thus we do not need to discuss this issue any further.

To obtain the exact solution of (68)-(69), we must apply the inverse Laplace transformation on (73)-(74). For that we have to apply some algebraic manipulations.

For the first case, let us assume that $v_j \neq v_k$ and $\lambda_j \neq \lambda_k$ for $j \neq k$ and $\forall j, k = 1, \ldots, m$. Then we can denote

$$\lambda_{kj} = \lambda_{jk} := \frac{\lambda_j - \lambda_k}{v_j - v_k} \,. \tag{75}$$

Furthermore, for the next transformation, we require that the values $\lambda_{jk}$ are different for each pair of indices $j$ and $k$.

The factors $\Lambda_{j,i}$ with $\lambda_j \neq \lambda_k$ for $j \neq k$ and the factor $\Lambda_{jk,i}$ with $\lambda_{jk} \neq \lambda_{jl}$ for $k \neq l$ are given by

$$\Lambda_{j,i,p} = \left( \prod_{\substack{k=p \\ k \neq j}}^{i} \frac{1}{\lambda_k - \lambda_j} \right) \,, \quad \Lambda_{jk,i,p} = \left( \prod_{\substack{l=p \\ l \neq j \\ l \neq k}}^{i} \frac{\lambda_{jl}}{\lambda_{jl} - \lambda_{jk}} \right) \,, \tag{76}$$

where we have the following assumptions:

$$1.\ v_j \neq v_k \ \ \forall j, k = 1, \ldots, m, \text{ for } j \neq k \,, \tag{77}$$

$$2.\ \lambda_j \neq \lambda_k \ \ \forall j, k = 1, \ldots, m, \text{ for } j \neq k \,, \tag{78}$$

$$3.\ \lambda_{jk} \neq \lambda_{jl} \ \ \forall j, k, l = 1, \ldots, m, \text{ for } j \neq k \ \wedge j \neq l \wedge k \neq l, \tag{79}$$

$$4.\ v_j \neq v_k \text{ and } \lambda_j \neq \lambda_k \ \ \forall j, k = 1, \ldots, m, \text{ for } j \neq k \,. \tag{80}$$

From (76), the last term in (73)-(74) for a given index $j$ can be rewritten in the following form,

$$\prod_{\substack{k=p \\ k \neq j}}^{i} \left( s(v_k - v_j) + \lambda_k - \lambda_j \right)^{-1} = \Lambda_{j,i,p} \sum_{\substack{k=p \\ k \neq j}}^{i} \frac{\lambda_{jk}}{s + \lambda_{jk}} \Lambda_{jk,i,p} \,. \tag{81}$$

From (70) adopted in (68) and (69), the standard inverse Laplace transformation can be used and the solution $u_i$ for (67) is given by

$$u_1(x,t) = \exp(-\lambda_1 t) \sum_{q=1}^{Q} \begin{cases} 0 & , 0 \leq x < v_1 t + x_q \\ b_{1,q}(x - v_1 t) + c_{1,q} & , v_1 t + x_q \leq x < v_1 t + x_{q+1} \\ 0 & , v_1 t + x_{q+1} \leq x \end{cases} , \tag{82}$$

$$u_i(x,t) = \exp(-\lambda_i t) \sum_{q=1}^{Q} \begin{cases} 0 & , 0 \leq x < v_i t + x_q \\ b_{i,q}(x - v_1 t) + c_{i,q} & , v_i t + x_q \leq x < v_i t + x_{q+1} \\ 0 & , v_i t + x_{q+1} \leq x \end{cases} \tag{83}$$

$$+\sum_{p=1}^{i-1} \Lambda_{i,p} \left( \sum_{j=p}^{i} \exp(-\lambda_j t) \Lambda_{j,i,p} \sum_{\substack{k=p \\ k\neq j}}^{i} \Lambda_{jk,i,p} A_{jk,p} \right) , \tag{84}$$

$$A_{jk,p} = \sum_{q=1}^{Q} \begin{cases} 0 & , 0 \le x < v_j t + x_q \\ b_{i,q}(x - (v_j t + x_i)) & \\ +(c_{i,q} - \frac{b_{i,q}}{\lambda_{jk}}) & \\ \cdot(1 - \exp(-\lambda_{jk}(x - (v_j t + x_q)))) & , v_j t + x_q \le x < v_j t + x_{q+1} \\ (c_{i,q} - \frac{b_{i,q}}{\lambda_{jk}} + b_{i,q}) & \\ \cdot \exp(-\lambda_{jk}(x - (v_j t + x_{q+1}))) & \\ -(c_{i,q} - \frac{b_{i,q}}{\lambda_{jk}}) & \\ \cdot \exp(-\lambda_{jk}(x - (v_j t + x_q))) & , v_j t + x_{q+1} \le x \end{cases}$$

with $i = 2, \ldots, m$.

where $Q$ is the number of piecewise linear intervals.

*Remark 4.* Here, we have derived analytical solutions of (64) with general initial conditions (65) that are used to verify numerical results or design discretization methods with embedded analytical support functions, see [17] and [32]. Modifications of the solutions can be done respecting to dominant components and improved notations to stabilize the numerical computations.

### 3.4 Solution for the mobile and immobile parts

Here we construct semi-analytical solutions for the mobile and immobile parts. We deal with the equations:

$$\partial_t u_i + v_i \partial_x u_i = -\lambda_i u_i + \lambda_{i-1} u_{i-1} + \beta(-u_i + g_i) , \tag{85}$$

$$\partial_t g_i = -\lambda_i g_i + \lambda_{i-1} g_{i-1} + \beta(-g_i + u_i) , \tag{86}$$

We propose a splitting method to decouple the mobile and the immobile parts of the equations.

We set $A$ as the operator for the mobile part and $B$ as the operator for the immobile part.

The following iteration scheme solves the problem.

**The iterative time-splitting method**

The following algorithm is based on the iteration with fixed splitting discretization step-size $\tau$. On the time interval $[t^n, t^{n+1}]$ we solve the following sub-problems consecutively for $j = 0, 2, \ldots 2m$.

$$\frac{\partial U_j(x,t)}{\partial t} = A U_j(x,t) \ + \ B U_{j-1}(x,t), \text{ with } \ U_j(t^n) = U^n \tag{87}$$

$$
\begin{aligned}
&U_0(x,t^n) = U^n \ , \ U_{-1} = 0, \\
&\text{and } U_j(x,t) = U_{j-1}(x,t) = u_1 \ , \text{ on } \partial\Omega \times (0,T) \ , \\
&\frac{\partial U_{j+1}(x,t)}{\partial t} = \ AU_j(x,t) \ + \ BU_{j+1}(x,t), \\
&\text{with } \ U_{j+1}(x,t^n) = U^n \ , \\
&\text{and } U_j(x,t) = U_{j-1}(x,t) = U_1 \ , \text{ on } \partial\Omega \times (0,T) \ ,
\end{aligned}
\tag{88}
$$

where $U^n = (u, g)^t$ is the vector of the mobile and immobile solutions and is the known split approximation at the time level $t = t^n$ (see [8]).

*Remark 5.* We can generalize the iterative-splitting method to a multi-iterative splitting method by introducing new splitting operators, e.g. spatial operators. Then we obtain multi-indices to control the splitting process. Each iterative splitting method can be solved independently, while connecting with further steps to the multi-splitting methods. In the following we introduce the multi-iterative-splitting method for a combined time-space-splitting method.

### 3.5 Computation of the mass for the discretization method

An application of the analytical solutions is the calculation of mass in an one-dimensional cell at time point $t$.

The integration of the analytical solutions is called mass. The integration is realized over the unit integral and afterwards in the application scaled on the mass of the finite volume cell.

The mass, that remains in the interval after a time point is calculated, as well as the mass that flowed out of the interval. The first mass $m_{i1}$, called residual mass, is calculated over the interval $(0, 1)$, and the second mass $m_{i2}$, called outflowing mass, is calculated over the interval $(1, \infty)$. The index $i$ denotes the component, where $i = 1, \ldots, m$.

We use the following approach to derive the mass:

- Calculating the residual mass in the interval $(0, 1)$.
- Calculating the total mass in the interval $(0, \infty)$.
- Calculating the outflowing mass in the interval $(1, \infty)$.

Subsequently, the mass is calculated step by step.

The integration over the intervals can be simplified by use of additive notation of the solution from equation (8). The notation is given by:

$$
\begin{aligned}
u_i(x,t) &= \sum_{j=1}^{i} u_{ij}(x,t), \\
u_{ij}(x,t) &= \ \Lambda_i \Big( \exp(-\lambda_j t) \ \Lambda_{j,i} \sum_{\substack{k=1 \\ k \neq j}}^{i} \Lambda_{jk,i} A_{jk} \Big).
\end{aligned}
\tag{89}
$$

The functions $\Lambda_i$, $\Lambda_{j,i}$, and $\Lambda_{jk,i}$ are declared in equations (25), (26), and (27).

Subsequently, for the sake of simplicity the functions are written as $m_{i1}(t) = m_{i1}$ and $m_{i2}(t) = m_{i2}$, respectively.

Afterwards the mass $m_{i1}$ is calculated over the interval $(0, 1)$. The intervals are ascertained for the domains of sub-equation (89). With this the integration boundaries are declared for every component $j$ in the interval $(v_j t, 1)$.

The integration is done in the subsequent equation in the space variable $x$.

### 3.6 Calculation of the residual mass

We now consider the calculation of mass that remains in the interval $(0, 1)$.

**Case** $i = 1$:

$$\begin{aligned} m_{11} &= \exp(-\lambda_1 t) \int_{v_1 t}^{1} (a(x - v_1 t) + b)\, dx \\ &= \exp(-\lambda_1 t)(a\frac{(1 - v_1 t)^2}{2} + b(1 - v_1 t)). \end{aligned} \tag{90}$$

**Case** $i = 2, \ldots, m$:

$$\begin{aligned} m_{i1} &= \int_0^1 u_i(x,t)dx = \int_{\min_{k=1}^{i}\{v_k t\}}^{1} u_i(x,t)\, dx \\ &= \int_{\min_{k=1}^{i}\{v_k t\}}^{1} \sum_{j=1}^{i} u_{ij}(x,t)\, dx \\ &= \sum_{j=1}^{i} (\int_{v_j t}^{1} u_{ij}(x,t)\, dx) \\ &= \Lambda_i \Bigg( \sum_{j=1}^{i} \exp(-\lambda_j t) \Lambda_{j,i} \sum_{\substack{k=1 \\ k \neq j}}^{i} \Lambda_{jk,i} \\ &\quad \cdot \int_{v_j t}^{1} \Big( a(x - v_j t) + (b - \frac{a}{\lambda_{jk}})(1 - \exp(-\lambda_{jk}(x - v_j t))) \Big) \Bigg) dx \\ &= \Lambda_i \Bigg( \sum_{j=1}^{i} \exp(-\lambda_j t) \Lambda_{j,i} \sum_{\substack{k=1 \\ k \neq j}}^{i} \Lambda_{jk,i} \\ &\quad \cdot \Bigg( a\frac{(1 - v_j t)^2}{2} \\ &\quad + (b - \frac{a}{\lambda_{jk}})((1 - v_j t) + \frac{1}{\lambda_{jk}}(\exp(-\lambda_{jk}(1 - v_j t)) - 1)) \Bigg) \Bigg). \end{aligned} \tag{91}$$

A further reformulation is realized for the notation depending on the interval.

Equation (91) is subdivided into four sub-equations, which are ordered according to the factors 1, $\frac{1}{\lambda_{jk}}$, $\frac{1}{\lambda_{jk}^2}$, and $\exp(\cdot)$. After rearrangement the following four sub-equations appear:

$$m_{i1} = m_{i1_1} + m_{i1_2} + m_{i1_3} + m_{i1_4}, \tag{92}$$

$$m_{i1_1} = \Lambda_i \Bigg( \sum_{j=1}^{i} \exp(-\lambda_j t)\ \Lambda_{j,i} \sum_{\substack{k=1 \\ k\neq j}}^{i} \Lambda_{jk,i} \cdot \left( a\frac{(1-v_j t)^2}{2} + b(1-v_j t) \right) \Bigg), \tag{93}$$

$$m_{i1_2} = \Lambda_i \Bigg( \sum_{j=1}^{i} \exp(-\lambda_j t)\ \Lambda_{j,i} \sum_{\substack{k=1 \\ k\neq j}}^{i} \Lambda_{jk,i} \cdot \left( -a\frac{1}{\lambda_{jk}}(1-v_j t) - b\frac{1}{\lambda_{jk}} \right) \Bigg), \tag{94}$$

$$m_{i1_3} = \Lambda_i \Bigg( \sum_{j=1}^{i} \exp(-\lambda_j t)\ \Lambda_{j,i} \sum_{\substack{k=1 \\ k\neq j}}^{i} \Lambda_{jk,i} \frac{a}{\lambda_{jk}^2} \Bigg), \tag{95}$$

$$m_{i1_4} = \Lambda_i \Bigg( \sum_{j=1}^{i} \exp(-\lambda_j t)\ \Lambda_{j,i} \sum_{\substack{k=1 \\ k\neq j}}^{i} \Lambda_{jk,i} \cdot (b - \frac{a}{\lambda_{jk}}) \frac{1}{\lambda_{jk}} \exp(-\lambda_{jk}(1-v_j t)) \Bigg). \tag{96}$$

From the additivity of the terms a remodeling can be realized.
Subsequently equations (93) – (96) are simplified.
Equations (93) – (95) are also simplified as follows:

$$\begin{aligned} m_{i1_1} &= \Lambda_i \Bigg( \sum_{j=1}^{i} \exp(-\lambda_j t)\ \Lambda_{j,i} \cdot \left( a\frac{(1-v_j t)^2}{2} + b(1-v_j t) \right) \sum_{\substack{k=1 \\ k\neq j}}^{i} \Lambda_{jk,i} \Bigg) \\ &= \Lambda_i \Bigg( \sum_{j=1}^{i} \exp(-\lambda_j t)\ \Lambda_{j,i} \left( a\frac{(1-v_j t)^2}{2} + b(1-v_j t) \right) \Bigg), \end{aligned} \tag{97}$$

$$m_{i1_2} = \Lambda_i \Bigg( \sum_{j=1}^{i} \exp(-\lambda_j t)\ \Lambda_{j,i} \cdot \left( -a(1-v_j t) - b \right) \sum_{\substack{k=1 \\ k\neq j}}^{i} \Lambda_{jk,i} \frac{1}{\lambda_{jk}} \Bigg) \tag{98}$$

$$
\begin{aligned}
&= \Lambda_i \Bigg( \sum_{j=1}^{i} \exp(-\lambda_j t)\ \Lambda_{j,i} \Big( -a(1-v_j t) - b \Big) \sum_{\substack{k=1 \\ k\neq j}}^{i} \lambda_{jk} \Bigg), \\
m_{i1_3} &= \Lambda_i \Bigg( \sum_{j=1}^{i} \exp(-\lambda_j t)\ \Lambda_{j,i}\ a \sum_{\substack{k=1 \\ k\neq j}}^{i} \Lambda_{jk,i} \frac{1}{\lambda_{jk}^2} \Bigg) \qquad (99) \\
&= \Lambda_i \Bigg( \sum_{j=1}^{i} \exp(-\lambda_j t)\ \Lambda_{j,i}\ a \sum_{\substack{k=1 \\ k\neq j}}^{i} \Big( \frac{1}{\lambda_{jk}} \sum_{\substack{l\geq k \\ l\neq j}}^{i} \frac{1}{\lambda_{jl}} \Bigg).
\end{aligned}
$$

Sub-equations (97) and (98) can be simplified using

$$\sum_{\substack{k=1 \\ k\neq j}}^{i} \Big( \prod_{\substack{l=1 \\ l\neq k \\ l\neq j}}^{i} \frac{\lambda_{jl}}{\lambda_{jl} - \lambda_{jk}} \Big) = 1, \qquad (100)$$

$$\sum_{\substack{k=1 \\ k\neq j}}^{i} \Big( \prod_{\substack{l=1 \\ l\neq k \\ l\neq j}}^{i} \frac{\lambda_{jl}}{\lambda_{jl} - \lambda_{jk}} \Big) \frac{1}{\lambda_{jk}} = \sum_{\substack{k=1 \\ k\neq j}}^{i} \frac{1}{\lambda_{jk}}. \qquad (101)$$

For equation (99) we use the following remodeling:

$$\sum_{\substack{k=1 \\ k\neq j}}^{i} \Big( \prod_{\substack{l=1 \\ l\neq k \\ l\neq j}}^{i} \frac{\lambda_{jl}}{\lambda_{jl} - \lambda_{jk}} \Big) \frac{1}{\lambda_{jk}^2} = \sum_{\substack{k=1 \\ k\neq j}}^{i} \Big( \frac{1}{\lambda_{jk}} \sum_{\substack{l\geq k \\ l\neq j}}^{i} \frac{1}{\lambda_{jl}} \Big), \qquad (102)$$

and the proof of the equality can be realized by induction.

Subsequently, equation (96) is simplified by remodeling into symmetrical terms that pairwise cancel themselves out.

There holds the following notation for equation (96):

$$
\begin{aligned}
m_{i1_4} &= \prod_{j=1}^{i-1} \lambda_j \sum_{j=1}^{i} \sum_{\substack{k=1 \\ k\neq j}}^{i} F_{jk} \\
&= \prod_{j=1}^{i-1} \lambda_j \sum_{j=1}^{i} \sum_{k>j}^{i} (F_{jk} + F_{kj}). \qquad (103)
\end{aligned}
$$

Factor $F_{jk}$ is given as:

$$
\begin{aligned}
F_{jk} = \exp(-\lambda_j t) &\Big( \prod_{\substack{k=1 \\ k\neq j}}^{i} \frac{1}{\lambda_k - \lambda_j} \Big) \Big( \prod_{\substack{l=1 \\ l\neq k \\ l\neq j}}^{i} \frac{\lambda_{jl}}{\lambda_{jl} - \lambda_{jk}} \Big) \qquad (104) \\
&\cdot \Big( b - \frac{a}{\lambda_{jk}} \Big) \frac{1}{\lambda_{jk}} \exp(-\lambda_{jk}(1 - v_j t)),
\end{aligned}
$$

where factor $F_{kj}$ emerges by interchange of the indices $j$ and $k$.

Subsequently we simplify equation (103). The pairwise factors $F_{jk}$ and $F_{kj}$ can be eliminated by

$$F_{jk} + F_{kj} = 0 \,, \quad \text{with } j = 1, \ldots, i \quad \text{and} \quad k > j. \tag{105}$$

Then there holds for term $m_{i1_4}$:

$$m_{i1_4} = 0. \tag{106}$$

The proof of equation (105) is subsequently presented.
The terms (104) are inserted in equation (105), and based on the equality the exp-functions are factorized. Then there holds:

$$F_{jk} + F_{kj} = \exp(-\lambda_j t) \left( b - \frac{a}{\lambda_{jk}} \right) \frac{1}{\lambda_{jk}} \cdot \tag{107}$$

$$\cdot \exp(-\lambda_{jk}(1 - v_j t))(\Lambda_{j,i}\Lambda_{jk,i} + \Lambda_{k,i}\Lambda_{kj,i}). \tag{108}$$

Using the statement $\Lambda_{j,i}\Lambda_{jk,i} + \Lambda_{k,i}\Lambda_{kj,i} = 0$, then there holds:

$$F_{jk} + F_{kj} = 0.0 \,. \tag{109}$$

For all $j = 1, \ldots, i$ and $k > j$ one obtains:

$$m_{i1_4} = 0. \tag{110}$$

Hence equation (106) is proved.

Equation (90) to calculate the mass can be written as:

$$m_{i1} = \Lambda_i \sum_{j=1}^{i} \Lambda_{j,i} \exp(-\lambda_j t) \left( a \frac{(1 - v_j t)^2}{2} + b(1 - v_j t - \sum_{\substack{k=1 \\ k \neq j}}^{i} \frac{1}{\lambda_{jk}}) \right.$$

$$\left. -a(1 - v_j t)(\sum_{\substack{k=1 \\ k \neq j}}^{i} \frac{1}{\lambda_{jk}}) + a\Big( \sum_{\substack{k=1 \\ k \neq j}}^{i} \frac{1}{\lambda_{jk}} (\sum_{\substack{l \geq k \\ l \neq j}}^{i} \frac{1}{\lambda_{jl}}) \Big) \right) . \tag{111}$$

In a further step the calculation of the total mass $m_{i_{tot}}$ is derived, which consists of the sub-masses $m_{i1}$ and $m_{i2}$.

### 3.7 Calculation of total mass

For the calculation it can be shown that the total mass consists of the mass of the pulse and the mass of the concentration of the ordinary differential equation.

For the total mass shall hold:

$$\begin{aligned} m_{i_{tot}} &= m_{pulse}\ c_{i,ODE} \\ &= m_{i1} + m_{i2}. \end{aligned} \tag{112}$$

This is shown subsequently in two steps.

**First Step**:

The total mass is calculated by means of the solution of the ordinary differential equation and the mass of the initial pulse: The total mass is calculated as follows:

$$\begin{aligned} m_{pulse} &= \int_{v_j t}^{1+v_j t} (a(x - v_j t) + b)\, dx \\ &= (a\frac{1}{2} + b), \\ c_{i,ODE} &= \Lambda_i \sum_{j=1}^{i} \Lambda_{j,i} \exp(-\lambda_j t), \\ m_{i,ODE} &= m_{pulse}\, c_{i,ODE} \\ &= (a\frac{1}{2} + b)\, \Lambda_i \sum_{j=1}^{i} \Lambda_{j,i} \exp(-\lambda_j t). \end{aligned} \tag{113}$$

The terms $\Lambda_i, \Lambda_{j,i}$, and $\Lambda_{jk,i}$ are declared in equations (15) and (19).

This completes the first step.

**Second Step**:

The total mass is now integrated over the total interval $(0, \infty)$.

For the total mass we have the following integral:

$$\begin{aligned} m_{i_{tot}} &= m_{i1}(t) + m_{i2}(t) \\ &= \int_{\min_{j=1}^{i}\{v_j t\}}^{1+\max_{j=1}^{i}\{v_j t\}} c_i(x,t)\, dx. \end{aligned} \tag{114}$$

For the integration we need the following considerations concerning the interval boundaries.

To consider all possibilities concerning the varying combination options for the integration boundaries we initiate the permutation group $k$ (cf. [27]). The values can be ordered as follows:
$v_{k(1)} < \ldots < v_{k(i)}$.

Without loss of generality we confine ourselves to a selection.
The selection is given as:

$$\begin{gathered} \text{W.l.o.g. holds:} \\ v_1 < v_2 \ldots < v_i. \end{gathered} \tag{115}$$

From the additivity of the solutions we can declare the individual sub-solutions as follows and utilize the integration boundaries. The upper integration boundary is given as $\max_{j=1}^{i}\{v_j t\} = v_i t$, and the integrals can be written as:

$$m_{i_{tot}} = \int_{\min_{j=1}^{i}\{v_j t\}}^{1+\max_{j=1}^{i}\{v_j t\}} c_i(x,t) dx \tag{116}$$

$$
\begin{aligned}
&= \sum_{j=1}^{i} \int_{v_j t}^{1+v_j t} c_{ij}(x,t)dx + \sum_{j=1}^{i-1} \int_{1+v_j t}^{1+v_i t} c_{ij}(x,t)\ dx \\
&= \ \Lambda_i \sum_{j=1}^{i} \ \Lambda_{j,i} \sum_{\substack{k=1 \\ k\neq j}}^{i} \Lambda_{jk,i} \exp(-\lambda_j t) \\
&\quad \int_{v_j t}^{v_j t+1} \left( a(x - v_j t) + (b - \frac{a}{\lambda_{jk}})(1 - \exp(-\lambda_{jk}(x - v_j t))) \right) dx \\
&+ \ \Lambda_i \sum_{j=1}^{i-1} \ \Lambda_{j,i} \sum_{\substack{k=1 \\ k\neq j}}^{i} \Lambda_{jk,i} \exp(-\lambda_j t) \\
&\quad \int_{v_j t+1}^{v_i t+1} \left( (b - \frac{a}{\lambda_{jk}} + a) \exp(-\lambda_{jk}(x - (v_j t + 1))) \right. \\
&\quad \left. -(b - \frac{a}{\lambda_{jk}}) \exp(-\lambda_{jk}(x - v_j t)) \right) dx.
\end{aligned}
$$

The integration is realized over the integration areas yielding the following solutions:

$$
\begin{aligned}
m_{i_{tot}} = \ & \Lambda_i \left( \sum_{j=1}^{i} \ \Lambda_{j,i} \sum_{\substack{k=1 \\ k\neq j}}^{i} \Lambda_{jk,i} \exp(-\lambda_j t) \right. \\
& \left. \left( a\frac{1}{2} + (b - \frac{a}{\lambda_{jk}})(1 + \frac{1}{\lambda_{jk}}(\exp(-\lambda_{jk}) - 1)) \right) \right) \\
+ \ & \Lambda_i \left( \sum_{j=1}^{i-1} \ \Lambda_{j,i} \sum_{\substack{k=1 \\ k\neq j}}^{i} \Lambda_{jk,i} \exp(-\lambda_j t) \right. \\
& \left( (b - \frac{a}{\lambda_{jk}} + a) \Big( - \frac{1}{\lambda_{jk}}(\exp(-\lambda_{jk}(v_i - v_j)t) - 1) \Big) \right. \\
& \left. \left. -(b - \frac{a}{\lambda_{jk}}) \Big( - \frac{1}{\lambda_{jk}}(\exp(-\lambda_{jk}((v_i - v_j)t + 1)) - \exp(-\lambda_{jk})) \Big) \right) \right).
\end{aligned} \tag{117}
$$

Some terms can be eliminated and equation and one obtains the following terms:

$$
\begin{aligned}
m_{i_{tot}}(t) = \ & \Lambda_i \sum_{j=1}^{i} \ \Lambda_{j,i} \exp(-\lambda_j t)(a\frac{1}{2} + b) \\
& + \ \Lambda_i \left( \sum_{j=1}^{i-1} \ \Lambda_{j,i} \sum_{\substack{k=1 \\ k\neq j}}^{i} \Lambda_{jk,i} \exp(-\lambda_j t) \right. \\
& \left( (b - \frac{a}{\lambda_{jk}} + a)(-\frac{1}{\lambda_{jk}} \exp(-\lambda_{jk}(v_i - v_j)t)) \right.
\end{aligned}
$$

$$-(b-\frac{a}{\lambda_{jk}})(-\frac{1}{\lambda_{jk}}\exp(-\lambda_{jk}((v_i-v_j)t+1)))\Bigg)\Bigg).$$

For the sake of simplicity we define the following terms of further considerations:

$$\tilde{F}_{jk} = \Lambda_{j,i}\Lambda_{jk,i}\exp(-\lambda_j t)\Bigg((b-\frac{a}{\lambda_{jk}}+a)(-\frac{1}{\lambda_{jk}}\exp(-\lambda_{jk}(v_i-v_j)t))\Bigg),$$

$$\hat{F}_{jk} = \Lambda_{j,i}\Lambda_{jk,i}\exp(-\lambda_j t)\Bigg((b-\frac{a}{\lambda_{jk}})(-\frac{1}{\lambda_{jk}}\exp(-\lambda_{jk}((v_i-v_j)t+1)))\Bigg).$$

For these terms we have the following statements:

$$\tilde{F}_{jk} + \tilde{F}_{kj} = 0, \tag{118}$$

$$\hat{F}_{jk} + \hat{F}_{kj} = 0, \tag{119}$$

$$\text{with } j = 1,\ldots,i \text{ and } j \neq k.$$

The proof can be done analogously by means of the statements of equation (112).

By eliminating the terms $\tilde{F}_{jk}$ and $\hat{F}_{jk}$ one obtains the equation for the total mass described as:

$$m_{i_{tot}} = \Lambda_i\left(\sum_{j=1}^{i}\Lambda_{j,i}\exp(-\lambda_j t)(a\frac{1}{2}+b)\right).$$

This concludes the second step, yielding the same result as in the first step. This proves the equality in equation (112).

Based on the simple calculation of the total mass $m_{i_{tot}}$ from Equation (112) a simpler calculation of the outflowing mass can be achieved.

This is considered subsequently in a further equation.

### 3.8 Calculation of the outflowing mass

From the statement of equation (112) the outflowing mass $m_{i2}$ can be calculated by:

$$m_{i2} = m_{i_{tot}} - m_{i1}.$$

This reduces the computational efforts significantly .

The next chapter describes the solver methods that are used for the implicitly discretized equation parts, especially those of the diffusion-dispersion equation.

## 4 Discretization Method

For the space-discretization we use finite volume methods and for the time-discretization we use explicit or implicit Euler methods. In the next section we introduce the notation for the space-discretization. Further, for the equation's terms we describe the discretization methods.

### 4.1 Notation

The time-steps for the calculation in the time-intervals are $(t^n, t^{n+1}) \subset (0, T)$ , for $n = 0, 1, \ldots$. The computational cells are given as $\Omega_i \subset \Omega$ with $j = 1, \ldots, I$. The unknown $I$ is the number of nodes.

For the use of finite volumes we have to construct the dual mesh for the triangulation $\mathcal{T}$ [11] of the domain $\Omega$. First, the finite elements for the domain $\Omega$ are given by $T^e, e = 1, \ldots, E$. The polygonal computational cells $\Omega_j$ are related to the vertices $x_j$ of the triangulation.

To get the relation between the neighbor cells and to use the volume of each cell we introduce the following notation. Let $V_j = |\Omega_j|$ and the set $\Lambda_j$ denote the neighbor-point $x_k$ to the point $x_j$. The boundary of cells $j$ and $k$ is $\Gamma_{jk}$.

We define the flux over the boundary $\Gamma_{jk}$ as

$$v_{jk} = \int_{\Gamma_{jk}} \mathbf{n} \cdot \mathbf{v} \, ds \, . \tag{120}$$

The inflow-flux is given as $v_{jk} < 0$, and the outflow-flux is $v_{jk} > 0$. The fluxes' antisymmetrics are denoted as $v_{jk} = -v_{kj}$. The total outflow-flux is given by:

$$\nu_j = \sum_{k \in out(j)} v_{jk}. \tag{121}$$

The idea of the finite volumes is to construct an algebraic equation system to express the unknowns $c_i^n \approx c(x_i, t^n)$. The initial values are given by $c_i^0$. The expression of the interpolation schemes could be given naturally in two ways. The first is given with the primary mesh of the finite elements:

$$c^n = \sum_{i=1}^{I} c_i^n \phi_i(x) \tag{122}$$

where $\phi_i$ are the standard globally-finite-element-basis functions [11]. The second possibility is for the finite volumes with:

$$\hat{c}^n = \sum_{i=1}^{I} c_i^n \varphi_i(x) \tag{123}$$

where $\varphi_i$ are piecewise constant discontinuous functions defined by $\varphi_i(x) = 1$ for $x \in \Omega_i$ and $\varphi_i(x) = 0$ otherwise.

### 4.2 Discretization of the convection equation with first-order

The piecewise constant discretization of the convection equation

$$\partial_t R \, c - \mathbf{v} \cdot \nabla c = 0 \, , \tag{124}$$

with the simple boundary condition $c = 0$ for the inflow and outflow boundary. We use the upwind discretization performed in [11] and get

$$V_j \; R \; c_j^{n+1} = c_j^n (R \; V_j - \tau^n \nu_j) + \tau^n \sum_{k \in in(j)} R \; c_k^n \; v_{kj} \; , \tag{125}$$

Because of the explicit discretization for time and to fulfill the discrete minimum-maximum property [11], we get a restriction for the time-steps as follows:

$$\tau^j = \frac{R \; V_j}{\nu_j} \; , \quad \tau^n \leq \min_{j=1,\ldots,I} \tau_j \tag{126}$$

In the next subsection we improve the discretization with a reconstruction with linear polynomes. The reconstruction is based on Godunov's method and is the limiter on the local minimum-maximum property.

### 4.3 Discretization of the convection equation with higher-order

The reconstruction was done in a previous paper [11] and we introduce the scheme in the next steps.

The linear polynomes are reconstructed over the element-wise gradient and are given as:

$$u^n(x_j) = c_j^n \; , \tag{127}$$

$$\nabla u^n|_{V_j} = \frac{1}{V_j} \sum_{e=1}^{E} \int_{T^e \cap \Omega_j} \nabla c^n dx \; , \tag{128}$$

$$\text{with} \quad j = 1, \ldots, I \; .$$

The piecewise linear function is given by:

$$u_{jk}^n = c_j^n + \psi_j \nabla u^n|_{V_j} (x_{jk} - x_j) \; , \tag{129}$$

$$\text{with} \quad j = 1, \ldots, I \; ,$$

where $\psi_i \in (0, 1)$ is the limiter which has to fulfill the discrete minimum-maximum property.

The piecewise linear function is given by:

$$u_{jk}^n = c_j^n + \psi_j \nabla u^n|_{V_j} (x_{jk} - x_j) \; , \text{ with} \quad j = 1, \ldots, I \; ,$$

where $\psi_j \in (0, 1)$ is the limiter which has to fulfill the discrete minimum-maximum property, as described in [11].

We also use the limitation of the flux to get no overshooting when transporting the mass and to receive the maximal time-step.

We get the restriction for the concentration as:

$$\tilde{u}_{jk}^n = u_{jk}^n + \frac{\tau_j}{\tau^n} (c_j^n - u_{jk}^n) \; . \tag{130}$$

On the basis of all the previous schemes the discretization for the second-order is written in the form

$$RV_j c_j^{n+1} = RV_j c_j^n - \tau^n \sum_{k \in out(j)} \tilde{u}_{jk}^n v_{jk} + \tau^n \sum_{l \in in(j)} \tilde{u}_{lj}^n v_{lj} \ , \tag{131}$$

This discretization method is used for the next coupled discretization with the reaction equation.

### 4.4 Discretization of the convection-reaction equation with one-dimensional analytical solutions

We apply Godonov's method for the discretization, see [23], and enlarge it with the solution of convection-reaction equations. We reduce the equation to a one-dimensional problem, solve the equation exactly and transform the one-dimensional mass to the multi-dimensional equation.

The discretization of the equation:

$$\partial_t \ c_l + \nabla \cdot \mathbf{v}_l \ c_l = -\lambda_l \ c_l + \lambda_{l-1} \ c_{l-1}, \qquad \text{with } l = 1, \ldots, m \ . \tag{132}$$

The velocity vector $\mathbf{v}$ is normed by $R_l$. The initial conditions are given by $c_1^0 = c_1(x, 0)$ , else $c_l^0 = 0$ for $l = 2, \ldots, m$ and the boundary conditions are trivial $c_l = 0$ for $l = 1, \ldots, m$.

We first calculate the maximal time-step for cell $j$ and concentration $i$ with the use of the total outflow fluxes:

$$\tau_{i,j} = \frac{V_j \ R_i}{\nu_j} \ , \quad \nu_j = \sum_{j \in out(i)} v_{ij} \ .$$

We get the restricted time-step with the local time-steps of cells and their components:

$$\tau^n \leq \min_{\substack{i=1,\ldots,m \\ j=1,\ldots,I}} \tau_{i,j} \ .$$

The velocity of the discrete equation is given by:

$$v_{i,j} = \frac{1}{\tau_{i,j}} \ .$$

We calculate the analytical solution of the mass with equation (132) (see also Subsection **??**) and obtain:

$$\begin{aligned} m_{i,jk,out}^n &= m_{i,out}(a, b, \tau^n, v_{1,j}, \ldots, v_{i,j}, R_1, \ldots, R_i, \lambda_1, \ldots, \lambda_i) \ , \\ m_{i,j,rest}^n &= m_{i,j}^n \ f(\tau^n, v_{1,j}, \ldots, v_{i,j}, R_1, \ldots, R_i, \lambda_1, \ldots, \lambda_i) \ , \end{aligned}$$

whereby $a = V_j R_i (c^n_{i,jk} - c^n_{i,jk'})$ , $b = V_j R_i c^n_{i,jk'}$ and $m^n_{i,j} = V_j R_i u^n_i$ are the parameters. The linear impulse in the finite-volume cell is $c^n_{i,jk'}$ for the concentration on the inflow- and $c^n_{i,jk}$ for the concentration on the outflow-boundary of the cell $j$.

The discretization with the embedded analytical mass is calculated by:

$$m^{n+1}_{i,j} - m^n_{i,rest} = - \sum_{k \in out(j)} \frac{v_{jk}}{\nu_j} \, m_{i,jk,out} + \sum_{l \in in(j)} \frac{v_{lj}}{\nu_l} \, m_{i,lj,out} \ ,$$

whereby $\frac{v_{jk}}{\nu_j}$ is the re-transformation for the total mass $m_{i,jk,out}$ in the partial mass $m_{i,jk}$ . The mass in the next time-step is $m^{n+1}_{i,j} = V_j \ c^{n+1}_i$ and in the old time-step it is the rest mass for the concentration $i$. The proof is shown in [13]. In the next section we derive an analytical solution for the benchmark problem.

## 5 Numerical experiments

The numerical and analytical methods are programmed in our software package $R^3T$, described in [15], based on the software tool $ug$, described in [2]. In this paper we will focus on the experiments: a description of the tools is presented in [13].

### 5.1 First experiment: ascending retardation factors with four species

We use ascending parameters for the retardation factors. The retardation factors are given as $R_1 = 1, R_2 = 2, R_3 = 4, R_4 = 8$. The reaction factors are given as $\lambda_1 = 0.4, \lambda_2 = 0.3, \lambda_3 = 0.2, \lambda_4 = 0$.

See the results in Figure 1. The $L_1$-error and the convergence rate are given as follows:

| $l$ | $E^1_{L_1}$ | $\rho^1_{L_1}$ | $E^2_{L_1}$ | $\rho^2_{L_1}$ | $E^3_{L_1}$ | $\rho^3_{L_1}$ | $E^4_{L_1}$ | $\rho^4_{L_1}$ |
|---|---|---|---|---|---|---|---|---|
| 4 | 0.0 | | $1.71\ 10^{-3}$ | | $1.04\ 10^{-3}$ | | $2.407\ 10^{-4}$ | |
| 5 | 0.0 | $\infty$ | $8.61\ 10^{-4}$ | 0.989 | $5.28\ 10^{-4}$ | 0.978 | $1.22\ 10^{-4}$ | 0.98 |
| 6 | 0.0 | $\infty$ | $4.29\ 10^{-4}$ | 1.005 | $2.65\ 10^{-4}$ | 0.995 | $6.13\ 10^{-5}$ | 0.993 |
| 7 | 0.0 | $\infty$ | $2.14\ 10^{-4}$ | 1.003 | $1.31\ 10^{-4}$ | 1.016 | $3.07\ 10^{-5}$ | 0.997 |

**Table 1.** $L_1$-error for the ascending-retardation factors with the standard method.

To compare these results with the modified version we reproduce the same calculations and get the following results: We improved the convergence rates for the modified results. They tend to the second-order so that we achieve a second-order method for such results.

The next experiment is done with reciprocal parameters.

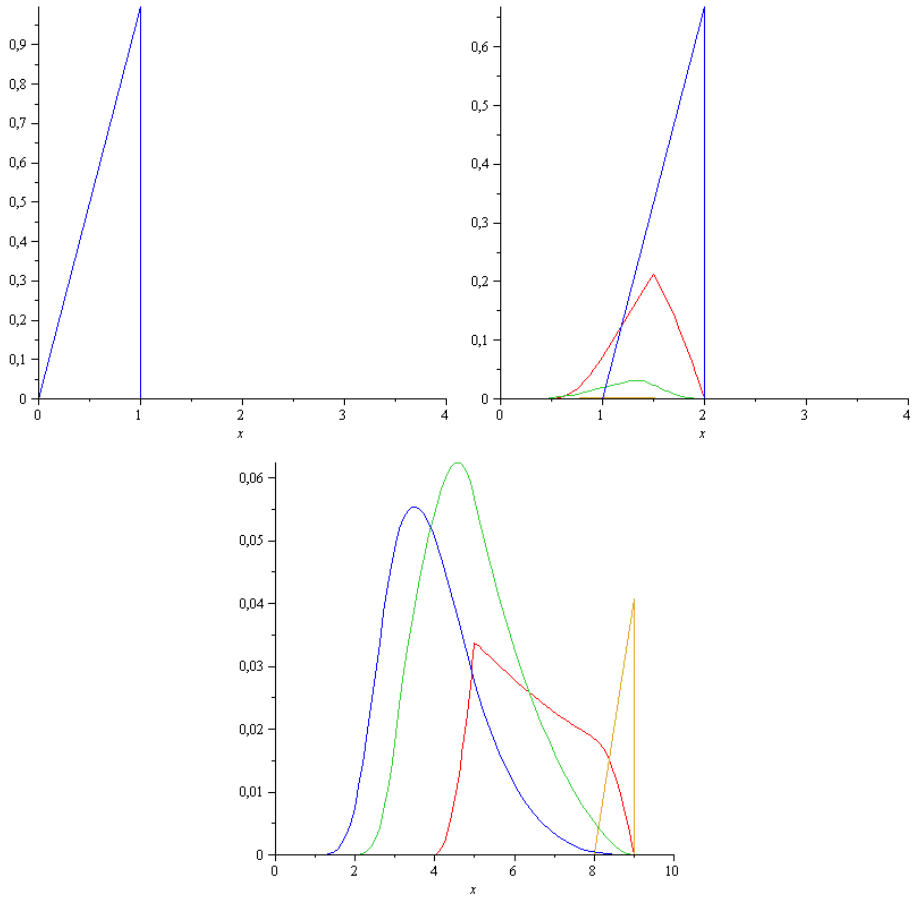


**Fig. 1.** Experiment ascending parameters.

### 5.2 Second experiment: descending retardation factor with five species

We use ascending parameters for the retardation factors. The retardation factors are given as $R_1 = 16, R_2 = 8, R_3 = 4, R_4 = 2, R_5 = 1$. The reaction factors are given as $\lambda_1 = 0.4, \lambda_2 = 0.3, \lambda_3 = 0.2, \lambda_4 = 0.1, \lambda_5 = 0.0$.

See the results in Figure 2. The results of the calculations are given as:

The modified example has the results:

The next experiment is done with ten species.

| $l$ | $E^1_{L_1}$ | $\rho^1_{L_1}$ | $E^2_{L_1}$ | $\rho^2_{L_1}$ | $E^3_{L_1}$ | $\rho^3_{L_1}$ | $E^4_{L_1}$ | $\rho^4_{L_1}$ |
|---|---|---|---|---|---|---|---|---|
| 4 | 0.0 | | $3.06\ 10^{-4}$ | | $3.91\ 10^{-5}$ | | $7.79\ 10^{-6}$ | |
| 5 | 0.0 | $\infty$ | $8.03\ 10^{-5}$ | 1.95 | $9.87\ 10^{-6}$ | 1.986 | $2.15\ 10^{-6}$ | 1.89 |
| 6 | 0.0 | $\infty$ | $2.007\ 10^{-5}$ | 2.0 | $2.60\ 10^{-6}$ | 1.93 | $5.81\ 10^{-7}$ | 1.89 |
| 7 | 0.0 | $\infty$ | $4.36\ 10^{-6}$ | 2.21 | $6.66\ 10^{-7}$ | 1.96 | $1.51\ 10^{-7}$ | 1.94 |

**Table 2.** $L_1$-error and convergence rate for the ascending-retardation factor done with the modified method

| $l$ | $E^1_{L_1}$ | $\rho^1_{L_1}$ | $E^2_{L_1}$ | $\rho^2_{L_1}$ | $E^3_{L_1}$ | $\rho^3_{L_1}$ | $E^4_{L_1}$ | $\rho^4_{L_1}$ |
|---|---|---|---|---|---|---|---|---|
| 4 | $7.30\ 10^{-3}$ | | $5.55\ 10^{-3}$ | | $1.069\ 10^{-2}$ | | $2.502\ 10^{-2}$ | |
| 5 | $2.57\ 10^{-3}$ | 1.58 | $2.27\ 10^{-3}$ | 1.25 | $5.16\ 10^{-3}$ | 1.051 | $1.225\ 10^{-2}$ | 1.02 |
| 6 | $9.36\ 10^{-4}$ | 1.53 | $1.01\ 10^{-3}$ | 1.16 | $2.52\ 10^{-3}$ | 1.033 | $6.056\ 10^{-3}$ | 1.01 |
| 7 | $3.52\ 10^{-4}$ | 1.45 | $4.73\ 10^{-4}$ | 1.09 | $1.24\ 10^{-3}$ | 1.023 | $3.00\ 10^{-3}$ | 1.01 |

**Table 3.** $L_1$-error and convergence rate for the descending-retardation factors for the standard method.

### 5.3 Third experiment: descending retardation factor with ten species

We use ascending parameters for the retardation factors. The retardation factors are given as $R_1 = 10, R_2 = 9, R_3 = 8, R_4 = 7, R_5 = 6 \ldots R_{10} = 1$. The reaction factors are given as $\lambda_1 = 2.0, \lambda_2 = 1.8, \lambda_3 = 1.6, \lambda_4 = 1.4, \ldots, \lambda_{10} = 0.0$.

With the assumptions:

- $\lambda_j \neq \lambda_k$
- $v_j \neq v_k$
- $\lambda_{jk} \neq \lambda_{jl}$

Here we apply the reduced equation 28 and 32.

The idea is to select the dominated decay chains and to apply them in the scheme.

We have the following color series: $u(1)$=red, $u(2)$=blue, $u(3)$=green, $u(4)$=yellow, $u(5)$=black, $u(6)$=cyan, $u(7)$=violet, $u(8)$=coral, $u(9)$=brown, $u(10)$=orange.

The results are given in Figures 3 and 4.

The next experiment is done with a two-dimensional benchmark problem.

### 5.4 Fourth experiment: rotating pyramid

For further applications of two-dimensional problems we focus on a new benchmark problem. The problem is described in the literature as a rotating Gaussian impulse, see [**?**].

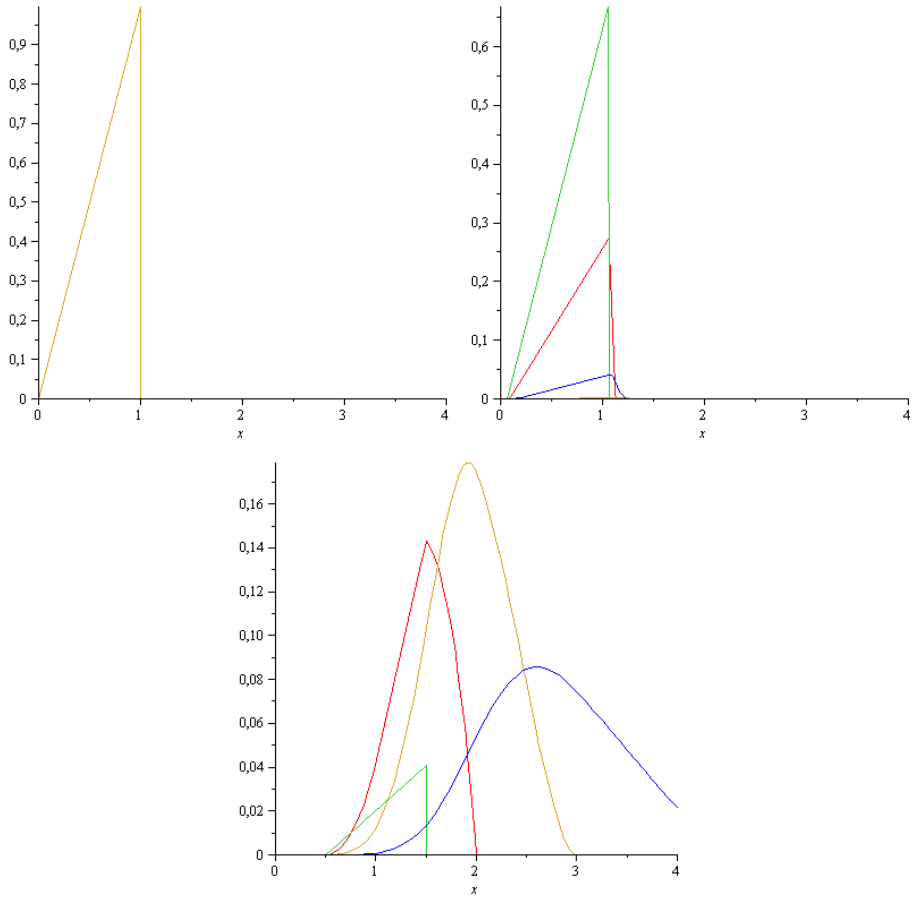


**Fig. 2.** Experiment descending parameters.

The application of our test example modified this benchmark problem in a form for use with the analytical one-dimensional solution.

The constant velocities are given on the circular lines and the continuous form of the impulse is given with a triangular impulse on the circular arc. The further directions are continuous on the radius $r$ with a linear function of $r$ beginning in the basic radius $r_a$ and $r_b$ as presented in Figure 5. Therefore the two-dimensional example is continuous in $\alpha$- and in $r$-direction.

The transformation changes the two-dimensional problem to a one-dimensional one, for which we derived the analytical solution.

The transformation from the Cartesian to the polar coordinates is given as:

$$r = \sqrt{x^2 + y^2}\ , \tag{133}$$

$$\epsilon(r) = r\ \alpha_0\ , \tag{134}$$

| $l$ | $E^1_{L_1}$ | $\rho^1_{L_1}$ | $E^2_{L_1}$ | $\rho^2_{L_1}$ | $E^3_{L_1}$ | $\rho^3_{L_1}$ | $E^3_{L_1}$ | $\rho^4_{L_1}$ |
|---|---|---|---|---|---|---|---|---|
| 4 | $7.30\ 10^{-3}$ | | $4.23\ 10^{-3}$ | | $1.43\ 10^{-3}$ | | $1.255\ 10^{-3}$ | |
| 5 | $2.57\ 10^{-3}$ | 1.58 | $1.14\ 10^{-3}$ | 1.89 | $3.07\ 10^{-4}$ | 2.22 | $2.82\ 10^{-4}$ | 2.15 |
| 6 | $9.36\ 10^{-4}$ | 1.53 | $2.49\ 10^{-4}$ | 2.24 | $7.94\ 10^{-5}$ | 1.95 | $6.81\ 10^{-5}$ | 2.05 |
| 7 | $3.52\ 10^{-4}$ | 1.45 | $5.82\ 10^{-5}$ | 2.11 | $2.04\ 10^{-5}$ | 1.96 | $1.68\ 10^{-5}$ | 2.02 |

**Table 4.** $L_1$-error and convergence rate for the descending-retardation factors done with the modified method.

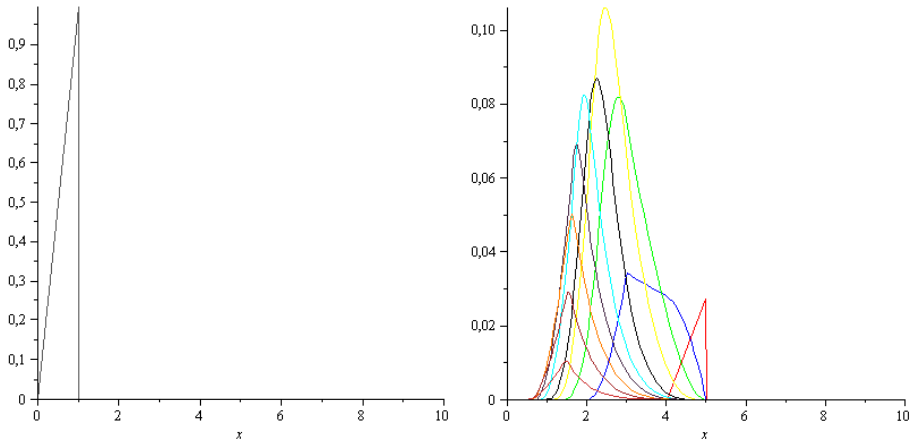


**Fig. 3.** Experiment with ten descending parameters (initial and experiment after $t = 4$).

the $(x, y) \in I\!R \times I\!R$ is the Cartesian coordinate, and $r$ is the radius, $\alpha_0$ is the initial arc and $\epsilon(r)$ is the length of the circular arc with radius $r$.

First, we transform the triangular impulse on the cylinder surface (see Picture 5). We receive a continuous impulse for one circle with radius $r$.

Second, we transfer the continuity in the $r$-direction with the dependency of the initial concentration $c_0(r)$, which depends on $r$. We reach further continuous triangular impulses for further circles, and the transformation is given as 135.

$$r_{med} = \frac{r_a + r_b}{2} \ , \tag{135}$$

$$c_0(r) = c_{init} \begin{cases} \frac{2}{r_b - r_a}(r - r_a) & r_a \le r \le r_{med} \\ \frac{-2}{r_b - r_a}(r - r_b) & r_{med} \le r \le r_b \\ 0.0 & sonst \end{cases} \ , \tag{136}$$

$c_{init} \in I\!R^+$ (Initial-concentration) .

The continuity in the $r$-direction is given in the vertical cut of the pyramid in the direction $r$ (see Figure 6).

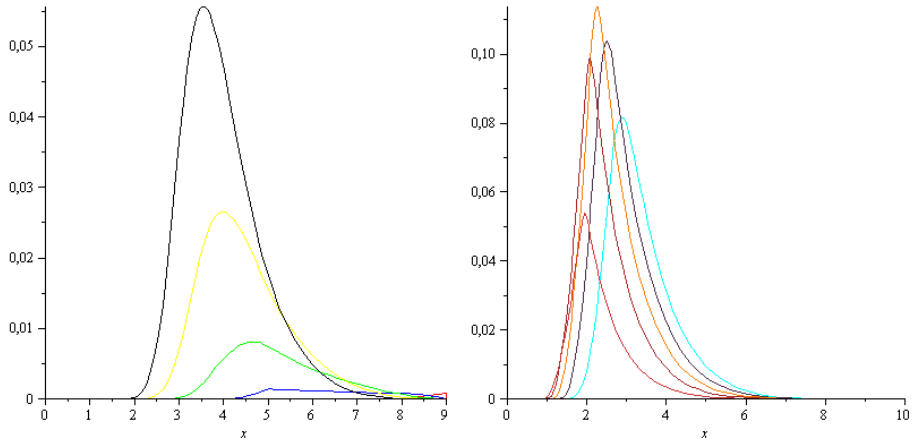


**Fig. 4.** Experiment with ten descending parameters (species 1-5 and species 6-10 after $t = 8$).

This initial impulse is then rotating on in the domain to follow the impulse, and the Cartesian domain is divided into four quadrants.

To use the analytical solution the rectangular domain is cut into four quadrants and the analytical solution is calculated with the polar coordinates (see Figure 7).

The arcs on each quadrants are given as:

$$\alpha = \begin{cases} arctan(|\frac{y}{x}|) & x < 0,\ y \leq 0 \\ arctan(|\frac{x}{y}|) + 0.5\pi & x \geq 0,\ y < 0 \\ arctan(|\frac{y}{x}|) + 1.0\pi & x > 0,\ y \geq 0 \\ arctan(|\frac{x}{y}|) + 1.5\pi & x \leq 0,\ y > 0 \end{cases} , \tag{137}$$

whereby the coordinates $(x, y)$ are in the domain $\Omega$.

Then we can calculate the length of the circular arc and it gives:

$$x_{arc}(r, \alpha) = r\ \alpha\ , \tag{138}$$

whereby $r$ is the radius to the point $(x, y)$ and $\alpha$ the arc, measured from the negative abscissa to the point $(x, y)$.

The velocity is given in the following form, divergence-free and orientated around the circle with:

$$\mathbf{v} = \begin{pmatrix} -4.0\ y \\ 4.0\ x \end{pmatrix} . \tag{139}$$

Therefore the velocity is constant on each circle and can be calculated with the radius $r$ by:

$$v = \sqrt{v_{rot,x}^2 + v_{rot,y}^2} = 4.0\ r\ , \tag{140}$$

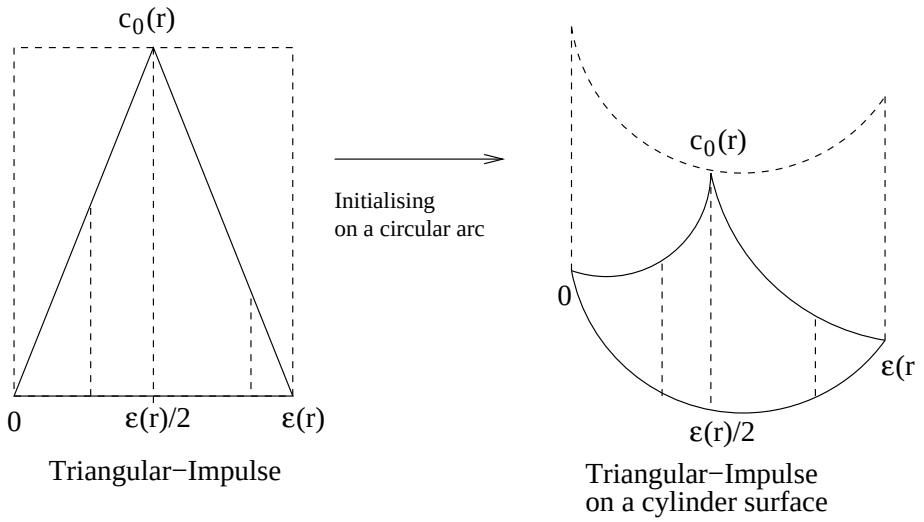


**Fig. 5.** The initializing of circular segments joined together results in a pyramid.

whereby $\mathbf{v} = (v_{rot,x}, v_{rot,y})^T$ is.

Then the one-dimensional analytical solution can be calculated.

The initializing for the rotating pyramid is calculated by:

$$u_{1,init} = u_{1,Tri}(x_{arc}(r, \alpha_0), t_0, \epsilon(r), c_0(r), v_1, \lambda_1) \ , \tag{141}$$

$$u_{i,init} = 0.0 \quad \text{with } i = 2, \ldots, M \ , \tag{142}$$

whereby $t_0 = 0.0$ bund $v_1 = \frac{v}{R_1}$ is. M is the number of components.

The analytical solution for an arbitrary time is given as:

$$u_{i,Tri} = u_{i,Tri}(x_{arc}(r, \alpha), t, \epsilon(r), c_0(r), v_1, \ldots, v_i, \lambda_1, \ldots, \lambda_i) \ , \tag{143}$$

whereby $i = 1, \ldots, M$ and $v_i = \frac{v}{R_i}$.

The example for the comparison is given with four components.

The parameters are given as: the porosity is $\phi = 0.5$, the retardation factor are:
$R_1 = 1.0,\ R_2 = 2.0,\ R_3 = 4.0,\ R_4 = 8.0$ and
the decay-rates are:
$\lambda_1 = 1.5,\ \lambda_2 = 1.4,\ \lambda_3 = 1.3,\ \lambda_4 = 0.0$ .

The initializing parameters are given as: height of the pyramid is $c_{init} = 1$, the base area in the polar coordinates is with the radius $0.125 \leq r \leq 0.375$ and with the initial arc $\alpha_0 = 0.22$.

The initial conditions are chosen to be sufficiently away from the boundary, so there is no influence from the boundary conditions.

The higher components are initialized with 0.0.

The initial condition of the first component is presented in Figure 8.

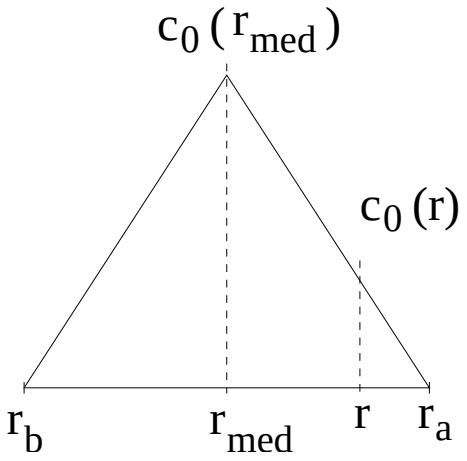


**Fig. 6.** Cut in $r$-direction off the pyramid.

The boundary conditions are trivial inflow and outflow conditions. There are no sources, i.d. $\tilde{Q}_i = 0.0$ for $i = 1, \ldots, 4$.

The domain is $[-0.5, 0.5] \times [-0.5, 0.5]$ and the coarse grid consists of one element, maximally refined till grid-level 7.

The time-steps are fixed at each level and fulfill the Courant number 0.5. The time-steps are halved for each finer grid-level.

The numerical results are calculated to the time-point $t = \frac{\pi}{4}$.

As in the previous example we calculated with the two methods and reached improved results in the modified method as presented in Table 5.

The Courant number was $\approx 0.5$ and we have a fixed time-step.

| $l$ | $E^1_{L_1}$ | $\rho^1_{L_1}$ | $E^2_{L_1}$ | $\rho^2_{L_1}$ | $E^3_{L_1}$ | $\rho^3_{L_1}$ | $E^4_{L_1}$ | $\rho^4_{L_1}$ |
|---|---|---|---|---|---|---|---|---|
| 4 | $7.12\ 10^{-3}$ | | $5.80\ 10^{-4}$ | | $3.09\ 10^{-5}$ | | $8.28\ 10^{-7}$ | |
| 5 | $2.74\ 10^{-3}$ | 1.377 | $2.14\ 10^{-4}$ | 1.44 | $1.12\ 10^{-5}$ | 1.46 | $2.86\ 10^{-7}$ | 1.53 |
| 6 | $1.10\ 10^{-3}$ | 1.32 | $8.82\ 10^{-5}$ | 1.27 | $4.90\ 10^{-6}$ | 1.19 | $1.20\ 10^{-7}$ | 1.25 |
| 7 | $4.40\ 10^{-4}$ | 1.322 | $3.50\ 10^{-5}$ | 1.33 | $1.90\ 10^{-6}$ | 1.37 | $4.80\ 10^{-8}$ | 1.32 |

**Table 5.** $L_1$-error and convergence rate for the modified method with an embedded analytical solution.

All components reached the second-order because there is no splitting error between the equations.

For this complex example we also obtained higher-order convergence results with the modified method.

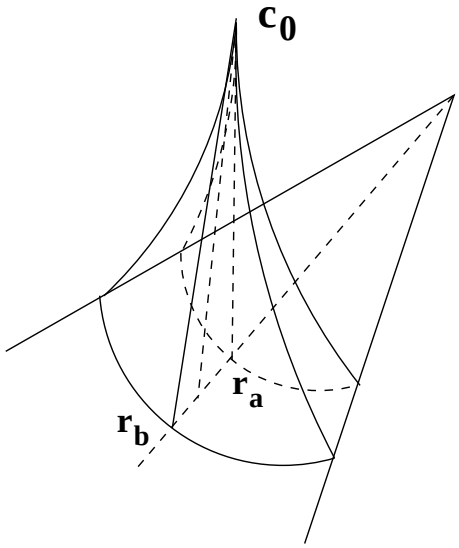


**Fig. 7.** Quadrants for the rotating pyramid.

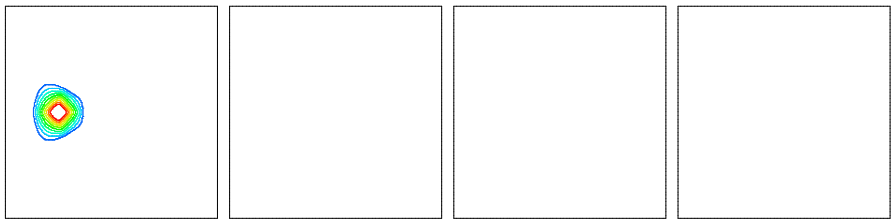

**Fig. 8.** Concentration of the first component at the initialization.

The results of the calculation to the end-point $t = \frac{\pi}{4}$ for the components are given in Figure 9.

The concentrations of the higher components are strongly retarded. The first component is transported furthest and rotated in the half circle. The successor components are enlarged to their predecessors' sizes. Therefore the characteristic results are fulfilled.

### 5.5 Realistic simulations

In the following subsections, we present our experiments based on the mobile and immobile gaseous phases. We contribute ideas for obtaining an optimal layer deposition, which is based on the PE-CVD process (Plasma-enhanced chemical vapor deposition), see [24].

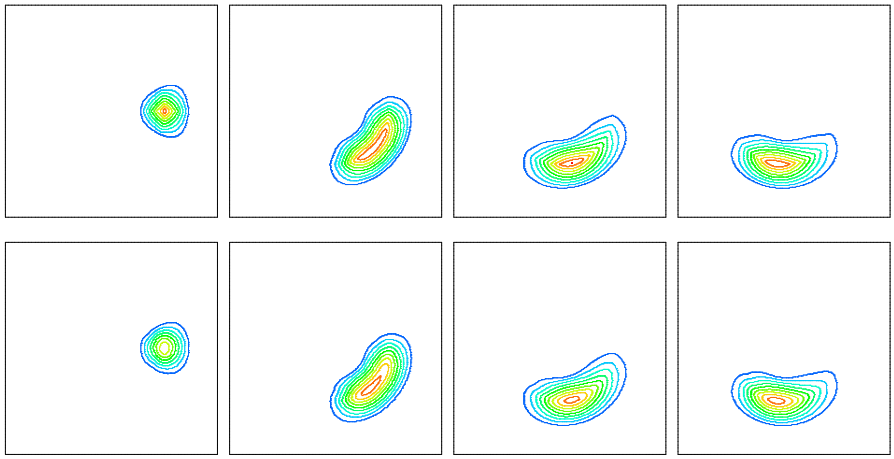

**Fig. 9.** The concentrations of the four components at the time-point $t = \frac{\pi}{4}$.

The main contributions are an optimal collection of point sources, line sources or moving sources to cover the deposition area. We simulate the deposition process with our fast decomposition algorithms and can deal with many different conditions that might be impossible for physical experiments. Such simulation results may benefit physical experiments and offer new ideas for optimizing such deposition problems.

The next experiments show the deposition rates for different sources and their optimal positions in the apparatus.

The experiments have the following outline:

The exchange between the mobile and immobile concentrations is very low: it is about $g = 10^{-14}$, and we assume less activities in the plasma environment. We apply a one-point source at the position $(50, 20)$. Our number of time-steps for the simulations is $\Delta t = 25$.

In Figure 10, we present the concentration of the one-point source with short time.

In Figure 11, we show the deposition rates of the immobile concentration and one-point source, with number of time-steps equal to 25.

In Figure 12, we show the deposition rates of the mobile concentration and one point source, with number of time-steps equal to 25.

*Remark 6.* The mobile concentrations are depositing as a heap, and here we can see the maximum concentration is at the point (50,0). The other concentrations in the neighborhood are much smaller; nevertheless the immobile concentration are very small owing to the mobile concentration. Therefore in the immobile phase we lost less of the deposition concentration.

## 6 Conclusions

We derived analytical solutions of convection dominant equations with general initial conditions. The analytical test functions are embedded to discretization methods for the convection diffusion reaction equation. Further mobile and immobile equations can be treated with decomposition methods that allow to reduce the computational complexity and obtain higher-order discretization schemes.

We could confirm also the new methods with the analytical and numerical test examples and present the higher-order results of the underlying schemes.

The problem for the convection-dominant equation can be solved with combined analytical and decomposed methods to decouple the complicated equation systems and achieve the accuracy with iterative or analytical embedded methods.

For complex computations of such convection-dominant problems, we use these methods in the initialization process of the computation and switch after sufficient accuracy to implicit methods with large time-steps.

In future the decomposition methods and analytically-improved methods can be generalized for non-smooth and non-linear problems in time and space.

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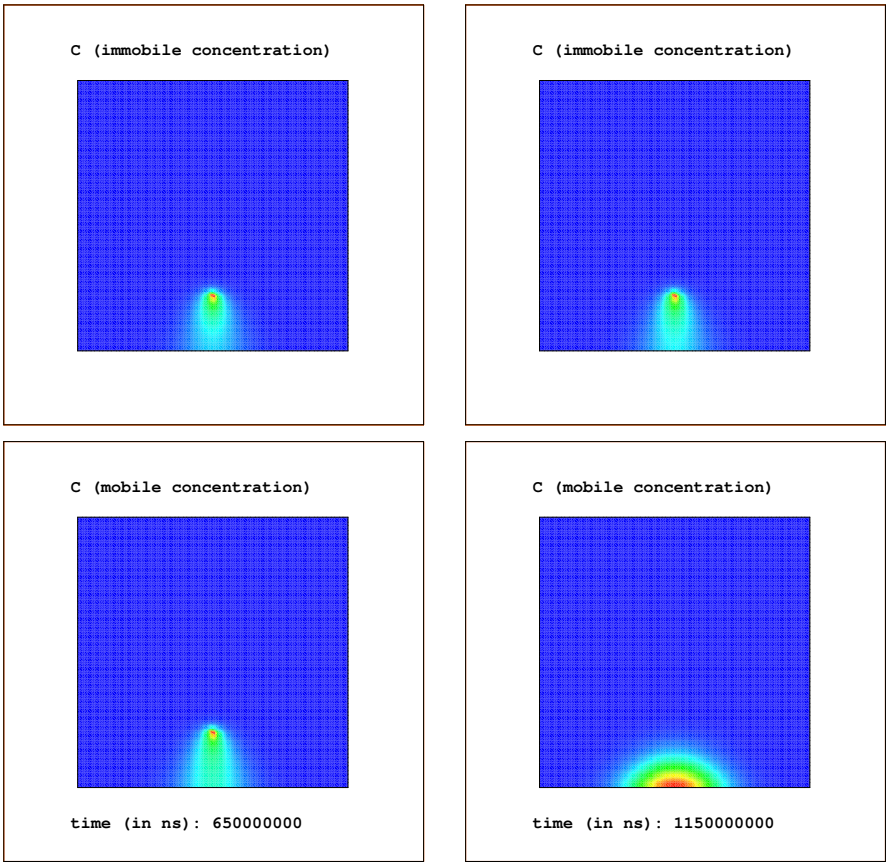


**Fig. 10.** One-point source, immobile and mobile cases, with number of time-steps equal to 25.

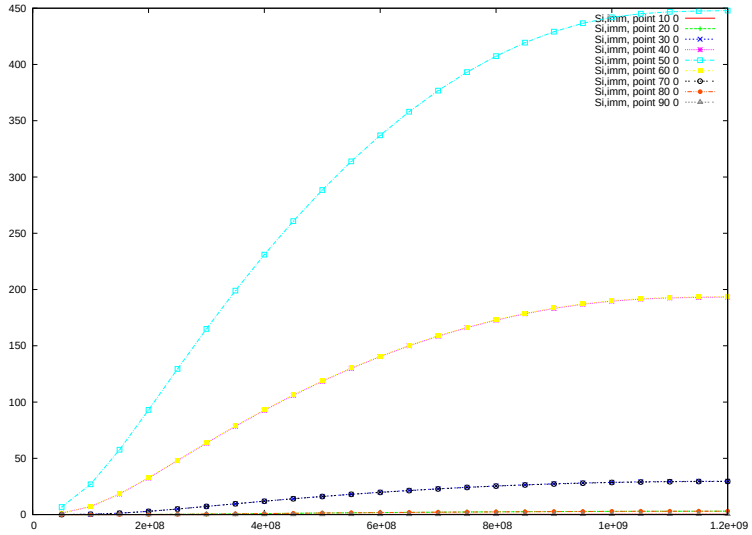


**Fig. 11.** Deposition rates in case of immobile concentration and one-point source, with number of time-steps equal to 25.

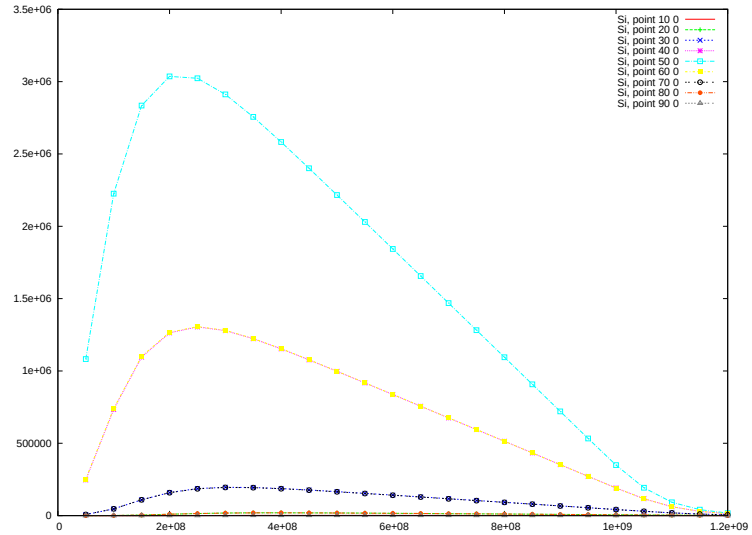


**Fig. 12.** Deposition rates in case of mobile concentration and one point source, with number of time-steps equal to 25.