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A fast numerical solution to the general mass-conservation equation for solutes and solids in aquatic sediments

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ABSTRACT

Mathematical modeling of species transformations in aquatic sediments is usually based on numerical solutions to the same general one-dimensional mass-conservation equation and is likely to require substantial computation time. In this paper we present a fast numerical solution to this equation. The solution is suited for both single and multi-component models and it is based on an implicit control volume discretization of the general mass-conservation equation. The solution consists of two algorithms, one that decomposes the discretization matrix once and one that subsequently produces multiple solutions with minimal computational effort. A unique feature of these algorithms is that values of boundary conditions can vary as a simulation progresses without requiring new decompositions of the discretization matrix. This feature can reduce computation time significantly relative to commonly used procedures for modeling dynamic systems. Finally, we present four examples in which the numerical solution is applied to specific problems. From these examples guidelines are derived for the discretization in space and time required to obtain precise solutions of the general mass-conservation equation.

1. Introduction

The numerical mathematical models that are being used extensively to study biogeochemical transformations in aquatic sediments typically rely on a one-dimensional mass-
conservation approach and include the vertical transport of one or more species. For example, many multi-component models have been published on organic matter and nutrient diagenesis (i.e., Rysgaard and Berg, 1996; Boudreau, 1996; Dhakar and Burdige, 1996; Soetaert et al., 1996; Van Cappellen and Wang, 1996; Luff et al., 2000; Berg et al., 2003; Meysman et al., 2003). Single-component models also generally require a numerical approach, for example as a tool to interpret measured concentration-depth profiles of $^{210}$Pb when estimating rates of sedimentation and bioturbation (i.e., Mulsow et al., 1998; Berg et al., 2001), or for extractions of production and consumption rates from measured concentration-depth profiles (i.e., Berg et al., 1998; Meile et al., 2001). A key element in all these studies is a numerical solution to the same general one-dimensional mass-conservation equation. The equation that includes transient and steady-state conditions, dissolved and solid species, solutes that adsorb onto the solid sediment, and the transport contributions by molecular diffusion, bioturbation (described as a diffusive process), irrigation (described as a non-local transport), and advection, yields

$$
(\xi \varphi + \rho_s (1 - \varphi) \kappa) \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( (\xi \varphi (D_{Bw} + D_s) + \rho_s (1 - \varphi) D_{Bs} \kappa) \frac{\partial C}{\partial x} \right) - \frac{\partial}{\partial x} \left( (\xi (\varphi u)_s + \rho_s (1 - \varphi) w) \xi \varphi C_0 - C \right) + (R_1 + R_2 C)
$$

where $\varphi$ is the porosity, $\rho_s$ is the density of the solid sediment, $C$ is the concentration, $t$ is the time, $x$ is the depth, $D_{Bw}$ is the biodiffusivity for solutes, $D_s$ is the molecular diffusivity corrected for tortuosity, $D_{Bs}$ is the biodiffusivity for solids, $u$ is the pore water velocity relative to the sediment-water interface, $w$ is the velocity of solids relative to the sediment-water interface, $\alpha$ is the irrigation coefficient, $C_0$ is the water column concentration, $R_1$ is the net production rate per unit volume of sediment, and $R_2$ is the rate constant for the first order production term. The parameters $\xi$ and $\kappa$ indicate whether the species is a solute ($\xi = 1, \kappa = 0$), a solid ($\xi = 0, \kappa = 1$), or a solute that adsorb to the solid sediment ($\xi = 1, \kappa = K'$ where $K'$ is the adsorption constant). Different biodiffusivities are defined for solutes and solids in Eq. 1 based on recent studies of Berg et al. (2001, 2003) indicating that the effects of bioturbation on solutes can be many fold stronger than on solids. Adsorption (and desorption) of solutes onto the solid sediment is included as a reversible process assumed to be in local equilibrium at any time in a depth-to-depth comparison. As a result of continuity conditions for the pore water and the solid fraction of the sediment ($\partial(\varphi u)/\partial x = 0, \partial((1 - \varphi) w)/\partial x = 0$), the products $\varphi u$ and $(1 - \varphi) w$ are constant with depth. As a result, each of the terms $\varphi u$ and $(1 - \varphi) w$ can be evaluated at any depth as indicated with the notation $(\cdot)_s$ in Eq. 1. For further details on Eq. 1, see for example Berner (1980) and Boudreau (1997).

Modeling of organic matter and nutrient diagenesis often requires significant computation times. For example, Van Cappellen and Wang (1996) ran their model on a SUN Sparc Station IPX which required 30 min to produce one single steady-state solution. Along the same lines, Luff et al. (2000) vectorized their code so it was suited to run on a CRAY
vector processor in order to reduce computation time. The fact that such models usually are run numerous times when applied to specific sediments or when used in analysis underscores the importance of choosing the numerical solution algorithm carefully. Models used as interpretation tools can also require substantial computational effort. For example, the procedure PROFILE (Berg et al., 1998) often simulates \(10^6\)-\(10^7\) independent steady-state profiles in the interpretation of a single measured concentration-depth profile.

This paper presents a numerical solution to Eq. 1 that is developed specifically to minimize computation time. The algorithm is suited to both single and multi-component models, and when utilized it can reduce computation time significantly relative to that of commonly used procedures. For that reason, it allows models as outlined above to be implemented on standard microcomputers (desktop and laptop computers) without resulting in prohibitive computation times.

2. Numerical solution

The numerical solution to Eq. 1 is based on a control volume approach (Patankar, 1980) and relies on a separation of the calculation domain into \(N\) control volumes each containing a grid point at its center (Fig. 1). It is assumed that the variation in space and time of concentration, \(C\), is described by piecewise continuous profiles which are uniquely determined when the grid point values of \(C\) are known. A discretization equation is derived using these profiles in an integration of Eq. 1 over a time step and a control volume. One clear advantage of this control volume approach is that mass-conservation is fulfilled exactly in the discretization equation.

a. Discretization equation

The user-defined control volumes comprising the calculation domain can vary with depth, allowing a fine resolution to be used near the sediment-water interface where the most pronounced gradients and second derivatives of concentrations are expected. The thickness of control volumes 1 and \(N\) are zero by definition (Fig. 1). If a diffusive boundary layer is included in the calculation domain, a control volume indexed \(M\) with a thickness of zero, marks the sediment-water interface. If this control volume separation is used for multi-component models involving both dissolved and solid species, solute concentrations are described for control volume 1 to \(N\) while concentrations of solids are found for control volume \(M\) to \(N\).

The integration of Eq. 1 over a time step, from time \(t\) to \(t + \Delta t\), and over control volume \(j\), from \(x_{j-1/2}\) to \(x_{j+1/2}\), yields

\[
\int_{x_{j-1/2}}^{x_{j+1/2}} \int_{t}^{t+\Delta t} H_1 \frac{\partial C}{\partial t} dt \, dx = \int_{x_{j-1/2}}^{x_{j+1/2}} \int_{t}^{t+\Delta t} \frac{\partial}{\partial x} \left( H_2 \frac{\partial C}{\partial x} - H_3 C \right) \, dx \, dt + H_4 (C_0 - C) + (R_1 + R_2 C) dt \, dx
\]

(2)
where

\[ H_1 = \xi \varphi + \rho_s (1 - \varphi) \kappa \]
\[ H_2 = \xi \varphi (D_{Bw} + D_s) + \rho_s (1 - \varphi) D_{Bw} \kappa \]
\[ H_3 = \xi (\varphi u)_i + \rho_s ((1 - \varphi) w)_i \kappa \]
\[ H_4 = \xi \varphi \alpha \]  

The variables \( H_1, H_2, \) and \( H_4 \) can vary with depth while \( H_3 \) as a result of continuity always will be constant with depth.

In order to perform the integration in Eq. 2, it is now assumed that \( H_1, H_2, H_3, H_4, R_1, \) and \( R_2 \) are constant throughout the time step and that the grid point values of \( H_1, H_4, R_1, \) and \( R_2 \) prevail throughout the control volume as representative mean values. The latter assumption is not needed for \( H_2 \) and \( H_3 \) because these variables are not integrated over the control volume. With these assumptions Eq. 2 gives
\[ H_1(C_j^{n+1} - C_j^n)\Delta x_j = \int_{t}^{t+\Delta t} \left( \left( H_2 \frac{\partial C}{\partial x} - H_3 C \right)_{j+1/2} - \left( H_2 \frac{\partial C}{\partial x} - H_3 C \right)_{j-1/2} \right) dt \]

\[ + (H_4(C_0 - C_j) + (R_{1j} + R_{2j}C_j))\Delta x_j \]  

where \( C_j^n \) is the old (known) grid point value of \( C \) at time \( t \), and \( C_j^{n+1} \) is the new (unknown) grid point value of \( C \) at time \( t + \Delta t \).

The second term on the right side of Eq. 4, \(-(H_2 \partial C/\partial x - H_3 C)_{j-1/2}\), represents the combined diffusive-advective flux, \( J_{j-1/2} \), over the boundary between control volume \( j-1 \) and \( j \) (Fig. 1). It has long been known that a straightforward central difference approximation of \( J_{j-1/2} \) inevitably leads to numerical instability when modeling advection-dominated systems (Courant et al., 1952). For that reason researchers have suggested approximations of \( J_{j-1/2} \) that ensure unconditionally stable schemes (i.e., Courant et al., 1952; Spalding, 1972; Fiadeiro and Veronis, 1977; Patankar, 1980, 1981; Berg, 1985). Some of the most successful schemes were derived as approximations to the analytical solution to the one-dimensional steady state mass-conservation equation accounting for transport by diffusion and advection. These schemes were defined through the 1970s and early 1980s and their success was evaluated not only in terms of how well they approximated this analytical solution but also how fast they could be evaluated numerically. Because computer processors have changed radically since then the relative utility of these evaluation schemes have changed as well. For this reason, we compare the performance of a selection of the most popular schemes on a modern microcomputer in Appendix A.

Common to all these schemes is the expression of flux, \( J_{j-1/2} \), as

\[ J_{j-1/2} = F_1C_j + F_2C_{j-1} \]  

and the individual schemes are defined through their definition of \( F_{1j} \) and \( F_{2j} \) which are derived in details for these schemes in Appendix A. Combining Eqs. 4 and 5 gives

\[ H_1(C_j^{n+1} - C_j^n)\Delta x_j = \int_{t}^{t+\Delta t} \left( -F_{1j+1}C_{j+1} - F_{2j+1}C_j + F_1C_j + F_2C_{j-1} \right) dt \]

\[ + (H_4(C_0 - C_j) + (R_{1j} + R_{2j}C_j))\Delta x_j \]  

When approximating the time integral in Eq. 6, it is necessary to assume how all the time-dependent terms vary from time \( t \) to \( t + \Delta t \). The time integral of \( C_j \) can be expressed as \((1 - \beta)C_j^n + \beta C_j^{n+1}\)\(\Delta t \) where \( \beta \) is a weighting factor, and different schemes will result depending on the value of \( \beta \). With \( \beta = 0 \), an explicit scheme is obtained, while \( \beta = 1 \) leads to an implicit scheme. With \( \beta = \frac{1}{2} \), the Crank-Nicolson scheme, a well-known hybrid of the explicit and the implicit scheme, is obtained. The implicit scheme is chosen here for the following reasons. Firstly, it leads to a versatile numerical solution allowing
transient solutions to be found using appropriately sized time steps, and at the same time, allowing steady-state solutions to linear problems to be produced with minimal computational effort in one large time step. Secondly, the implicit scheme is especially attractive in one-dimensional formulations when computation time is of concern. While the number of numeric operations per time step in the explicit, Crank-Nicolson, and implicit scheme is similar, a restrictive upper limit exists for the time steps in the explicit scheme. When violated, numerical instability occurs. For example, in diffusion-dominated systems this critical time step equals $\frac{1}{2} \Delta x^2 H_1/H_2$ where $H_1$ and $H_2$ are given by Eq. 3. In models of organic matter and nutrient diagenesis where oxygen usually is a key component that typically penetrates only a few mm into the sediments, a $\Delta x$ of $\sim 0.01$ cm is required to accurately describe the oxygen profile. With typical values of $H_1$ and $H_2$ of 0.8 and $10^{-5}$ cm$^2$ s$^{-1}$, the critical time step is 4 s for the explicit scheme. Such small time steps will lead to prohibitive computation times when multiple-year simulations are required. Upper limits to the time step obviously also exist for the implicit scheme in such simulations, but they are of a different nature and are generally markedly less restrictive. For example, in multi-component models, fast non-linear reactions between species can restrict the size of the time steps that can be used. However, in such modeling exercises, performed with realistic reaction rate constants, time steps on the order of 1 h are usually sufficient to ensure an accurate numerical solution as we demonstrate in an example below. As the result of the explicit element in the Crank-Nicolson scheme it can, depending on the application, also suffer from restrictive demands on the time step. As a simple example of this, it is not possible to produce steady-state solutions to linear problems in one large time step as is the case with the implicit scheme.

The implicit time integration in Eq. 6 gives

$$H_{1j}(C_{j+1}^{n+1} - C_j^n) \frac{\Delta x_j}{\Delta t} = -F_{1j+1} C_{j+1}^{n+1} - F_{2j+1} C_j^{n+1} + F_{1j} C_{j+1}^{n+1} + F_{2j} C_j^{n+1} + H_{4j}(C_0 - C_j^{n+1}) \Delta x_j + (R_{1j} + R_{2j} C_j^{n+1}) \Delta x_j$$

which gives the following tri-diagonal system of equations

$$AA_j C_{j+1}^{n+1} + BB_j C_j^{n+1} + CC_j C_{j+1}^{n+1} = DD_j$$

where the coefficients are defined as

$$AA_j = F_{2j}$$

$$BB_j = F_{1j} - F_{2j+1} - H_{4j} \Delta x_j + R_{2j} \Delta x_j - H_{1j} \frac{\Delta x_j}{\Delta t}$$

$$CC_j = -F_{1j+1}$$

$$DD_j = -H_{1j} \frac{\Delta x_j}{\Delta t} C_j^n - H_{4j} C_0 \Delta x_j - R_{1j} \Delta x_j$$

$$(9)$$
The control volume spanning $\Delta x_j$ is included deliberately as a factor in Eq. 9 rather than a denominator allowing $\Delta x_j$ to equal zero.

**b. Boundary conditions**

The boundary conditions that bring closure to the tri-diagonal system of equations (Eq. 7) are imposed implicitly through control volume $L$ and $N$, where $L$ equals either 1 or $M$ depending on how the calculation domain is separated into control volumes (Fig. 1). For control volume $L$ and $N$, Eq. 8 simplifies to

$$BB_L C_L^{n+1} + CC_L C_{L+1}^{n+1} = DD_L$$

and

$$AA_N C_{N-1}^{n+1} + BB_N C_N^{n+1} = DD_N.$$  (11)

The coefficients $BB_L$, $CC_L$, $DD_L$, $AA_N$, $BB_N$, and $DD_N$ are given values depending on the kind of boundary conditions imposed. Three types of boundary conditions are possible: a known concentration, a known flux, and a known concentration gradient. The assignment of values to $BB_L$, $CC_L$, $DD_L$, $AA_N$, $BB_N$, and $DD_N$ depending on the type and value of the boundary conditions are outlined in Table 1. The unique set of boundary concentrations, $C_L^{n+1}$ and $C_N^{n+1}$, which ensures that the desired boundary conditions are imposed, is obtained when the tri-diagonal system of equations (Eqs. 8, 10, 11) is solved.

**c. Solution of tri-diagonal system of equations**

Several models of biogeochemical transformations in aquatic sediments rely on implicit schemes. In these models, the tri-diagonal system of equations is typically solved by Gaussian elimination numerous times in a single simulation (i.e. Dhakar and Burdige, 1996; Van Cappellen and Wang, 1996) using for example the Thomas algorithm (i.e. Patankar, 1980; Huyakorn and Pinder, 1983). Rather than performing this straightforward
Gaussian elimination in every time step, a significant reduction in computation time can be obtained as follows.

The coefficient $DD_j$ in the tri-diagonal system of equations (Eq. 9, Table 1) will typically vary from time step to time step, in most applications simply because $DD_j$ contains the concentration $C_j^n$ at the old time level $t$. In contrast, the coefficients $AA_j$, $BB_j$ and $CC_j$ are likely to be constant throughout the simulation (Eq. 9, Table 1), or at least vary at such a slow rate that it is appropriate to treat them as constants through many consecutive time steps. An example of this is dynamic simulations based on time steps on the order of minutes and where much slower seasonal temperature variations will affect variables such as molecular diffusivities, and thus $AA_j$, $BB_j$ and $CC_j$. In such simulations, it is clearly a good approximation only to update or recalculate the coefficients $AA_j$, $BB_j$ and $CC_j$ on a weekly or monthly basis. This characteristic can be taken advantage of to reduce the computational effort significantly in successive solutions of the tri-diagonal system of equations by decomposing the discretization matrix only once, or only with time intervals where $AA_j$, $BB_j$ and $CC_j$ vary markedly. This is done by reformulating the Thomas algorithm.

The forward substitution in the Thomas algorithm where Eqs. 8, 10, and 11 are solved in the interval $L \leq j \leq N$ yields (i.e. Patankar, 1980; Huyakorn and Pinder, 1983)

$$
PP_L = -\frac{CC_L}{BB_L}; \quad QQ_L = \frac{DD_L}{BB_L}
$$

$$
PP_j = -\frac{CC_j}{BB_j + AA_j PP_{j-1}} \quad QQ_j = \frac{DD_j - AA_j QQ_{j-1}}{BB_j + AA_j PP_{j-1}} \quad (j = L + 1 \rightarrow N - 1)
$$

$$
QQ_N = \frac{DD_N - AA_N QQ_{N-1}}{BB_N + AA_N PP_{N-1}}
$$

where $PP_j$ and $QQ_j$ are decomposition variables and $AA_j$, $BB_j$, $CC_j$, and $DD_j$ are defined either by Eq. 9 or in Table 1. The following back substitution that gives the values of $C_j^{n+1}$ yields

$$
C_N^{n+1} = QQ_N
$$

$$
C_j^{n+1} = PP_j C_{j+1}^{n+1} + QQ_j \quad (j = N - 1 \rightarrow L)
$$

The significant gain in computational efficiency is now achieved by rewriting Eq. 12 so that $DD_j$ is kept out of the forward substitution by defining an additional decomposition variable $NN_j$ as follows:
With this modification the back substitution that gives the values of $C_j^{n+1}$ then yields

$$\begin{align*}
QQL &= DDLNNL \\
QQ_j &= (DD_j - AA_jQQ_{j-1})NN_j \quad (j = L + 1 \rightarrow N) \\
C_N^{n+1} &= QQ_N \\
C_j^{n+1} &= PP_jC_j^{n+1} + QQ_j \quad (j = N - 1 \rightarrow L)
\end{align*}$$

There are $5(N - L) + 1$ numeric operations in Eq. 15, approximately half the number used in the original Thomas algorithm $(10(N - L) - 1)$. Because multiplications are computationally less costly to perform than divisions, the overall result is that Eq. 15 are 2.5 times faster to execute than those of the original Thomas algorithm on a 2.0 GHz Pentium M PC.

Another important and unique feature of this numerical solution is that the type of boundary condition is introduced through $BB_L$, $CC_L$, $AA_N$, and $BB_N$ (Table 1) while the values of the boundary condition are imposed through $DD_L$ and $DD_N$. This characteristic allows the values of boundary conditions to vary as a simulation progresses without requiring new decompositions of the discretization matrix.

The coefficient $DD_j$ (Eq. 9) must be calculated in every time step. This is done most effectively as

$$DD_j = -EE_jC_j^n - FF_jC_0 - R_{1j}\Delta x_j$$

where $EE_j$ and $FF_j$ are defined as

$$EE_j = H_{1j} \frac{\Delta x_j}{\Delta t} \quad \text{and} \quad FF_j = H_{4j}\Delta x_j$$

which, with the definitions of $H_{1j}$ and $H_{4j}$ (Eq. 3), typically need only be evaluated once.

In summary, it is convenient to calculate the coefficients given by Eqs. 3, 9, and 17 and perform the new forward substitution given by Eq. 14 in one algorithm. We have named this algorithm CONSTANTS and its content is summarized in Appendix B. The algorithm includes five optional expressions for the molecular sediment diffusivity ($D_s$) as a function of porosity and diffusivity in water. The two first were originally defined by Ullman and Aller (1982), the third and fourth were given by Iversen and Jørgensen (1993), and the fifth
was defined by Boudreau (1997). The output from CONSTANTS are input to the second algorithm, CNEW, which performs the back substitution (Eq. 15) leading to the new concentrations every time it is utilized. The content of CNEW is summarized in Appendix C.

3. Applications and examples

The numerical solution, separated into the two algorithms CONSTANTS and CNEW, is rather versatile and can be used to simulate steady state, dynamic, linear, and nonlinear problems that further can involve one or more dissolved or solid species. The outlined features of the solution are particularly beneficial in applications where long computation times are of concern.

Four example applications of the algorithm are presented below, representing computational gains achieved in diverse problems. The first three focus on rather simple cases, for which analytical solutions exist. They also serve as a test of the numerical solution and as an illustration of the discretization in depth, (and in time for transient problems) required to obtain accurate solutions. In the last example, the solution is implemented in a dynamic, multi-component, and nonlinear model of organic matter and nutrient diagenesis in a specific sediment. This example illustrates clearly the significant advantages that can be achieved in terms of short computation times when applying the numerical solution to models where components with very different time constants require relatively small time steps combined with long simulation times to produce quasi-stationary solution on a year to year basis. All examples are coded in FORTRAN 90 and the simulations are performed in double precision.

a. Example 1

Four types of solute transport, molecular diffusion, bioturbation, irrigation, and advection, are represented in Eq. 1. An analytical solution to the equation is possible under steady-state conditions if advection and first-order production terms are neglected, and if $\varphi$, $D_s$, $D_{bw}$, $\alpha$, and $R_1$ are assumed to be constant with depth. Under these conditions Eq. 1 simplifies to

$$\varphi(D_{bw} + D_s) \frac{d^2 C}{dx^2} + \varphi \alpha (C_0 - C) + R_1 = 0$$

which has the solution

$$C = A \exp\left(-\frac{\alpha}{D_{bw} + D_s} x\right) + B \exp\left(\frac{\alpha}{D_{bw} + D_s} x\right) + \frac{\alpha C_0 + R_1}{\varphi}$$

where A and B are arbitrary constants (Boudreau 1997).

Berg et al. (1998) calculated a hypothetical O$_2$ profile in the depth interval from 0.05 to 1.0 cm assuming constant consumption rates ($R_1$) of 0.004 and 0.012 nmol cm$^{-3}$ s$^{-1}$ for the depth intervals of 0 to 0.75 and 0.75 to 1.0 cm and then applying Eq. 19 to each of these
intervals. In the diffusive boundary layer ($\delta_D$) from $-0.05$ to $0$ cm, the solution simplifies to a straight line. It was further assumed that the $O_2$ concentration equals 0 at 1 cm depths and below. Finally, values of $\varphi$, $D_{Bw}$, $D_s$, and $\alpha$, of $0.75$, $3 \times 10^{-6}$ cm$^2$ s$^{-1}$, $9 \times 10^{-6}$ cm$^2$ s$^{-1}$, and $5 \times 10^{-6}$ s$^{-1}$ were assumed by Berg et al. (1998). Here (Fig. 2A) we extended the solution to also include the depth interval of 1 to 1.25 cm for which Eq. 18 simplifies to $R_1 = -\varphi \alpha C_0$.

The $O_2$ profile was simulated repeatedly utilizing the algorithms CONSTANTS and CNEW while the number of equally spaced control volumes ($N$) was increased incrementally. The error of the numerical solution was determined as the maximum deviation in the $-0.05$ to 1.25 cm depth interval from the analytical solution in percent of the water column concentration (Fig. 2B). Since the numerical solution is fully implicit each simulated steady-state profile was determined in one single use of both CONSTANTS and CNEW in which an “infinitely large” time step ($1 \times 10^{-30}$ s) was specified. The error of the numerical solution declines rapidly with increasing $N$ (Fig. 2B) and errors $< 1$, 0.1, and 0.01% was found for $N$ equal to 10, 25, and 80. The local periodic variation of the error was caused by offsets between the abrupt changes in the imposed $O_2$ consumptions (Fig. 2A) and the boundaries between control volumes.

b. Example 2

Two types of solid transport, bioturbation and advection, are included in Eq. 1. An analytical solution to the equation is possible under steady-state conditions if zero order
production terms are neglected and if $\varphi$ is assumed to be constant with depth. Under these conditions Eq. 1 simplifies to

$$\frac{d}{dx} \left( D_{Bs} \frac{dC}{dx} \right) - w \frac{dC}{dx} + \frac{R_2}{\rho_s (1 - \varphi)} C = 0$$

(20)

This equation describes for example a radioactive tracer, such as $^{210}\text{Pb}$, that is supplied to a sediment surface at a constant rate, is transported to deeper sediment layers, and is disappearing through a first order decay. In this case the decay constant, $\lambda$, equals $-R_2/\rho_s (1 - \varphi)$. Swaney (1999) showed that if $D_{Bs}$ exhibits a parabolic decrease with depth as $D_{Bs} = D_{Bs_0} (1 - x/L)^2$, the analytical solution to Eq. 20 in the 0 to $L$ depth interval is

$$C = C_0 \sqrt{\frac{L}{L-x}} \exp\left( \frac{1}{2} Pe \frac{x}{(L-x)} \right) \frac{K_0\left( \frac{1}{2} Pe \frac{L}{(L-x)} \right)}{K_v\left( \frac{1}{2} Pe \right)}$$

(21)

where $C_0$ is the concentration at the sediment surface, $Pe$ is Peclet number equal to $wL/D_{Bs_0}$, and $K_v$ is the modified Bessel function of the order $\nu$ and of the second kind where $\nu = \sqrt{\lambda L^2/D_{Bs_0}} + \frac{1}{4}$. With values of $L$, $D_{Bs_0}$, $w$, and $\lambda$ of 10 cm, 0.05 cm$^2$ year$^{-1}$, 0.05 cm year$^{-1}$, and 0.0315 year$^{-1}$, a hypothetical $^{210}\text{Pb}$ profile was calculated from Eq. 21 (Fig. 3A). As in Example 1, the $^{210}\text{Pb}$ profile was simulated repeatedly for
increasing $N$ and the error of the numerical solution was determined as the maximum deviation in the 0 to 10 cm depth interval from the analytical solution in percent of the sediment surface concentration (Fig. 3B). Also in this example each numerical solution was found in one “infinitely large” time step ($1 \times 10^{30}$ s). The error of the numerical solution decreases with increasing $N$ (Fig. 3B), but not as pronounced as in Example 1. Errors of 1 and 0.1% were found for $N$ equal to 31 and 105.

**c. Example 3**

As an example of nonsteady-state conditions, a conservative dissolved tracer that is supplied to a sediment from the overlying water is considered. An analytical solution to Eq. 1 is possible if irrigation is neglected and it is assumed that $\varphi, D_s$, and $D_{bw}$ are constant with depth. Under these conditions Eq. 1 simplifies to

$$\frac{\partial C}{\partial t} = (D_{bw} + D_s) \frac{\partial^2 C}{\partial x^2} - u \frac{dC}{dx}$$

(22)

If the diffusive boundary layer is neglected and the tracer is absent in the sediment at time zero after which the tracer concentration is increased momentarily to a constant value at the sediment surface, the analytical solution to Eq. 22 is

$$C = \frac{1}{2} C_0 \left( \text{erfc} \left( \frac{x - ut}{2 \sqrt{(D_{bw} + D_s) t}} \right) + \exp \left( \frac{xu}{(D_{bw} + D_s)} \right) \text{erfc} \left( \frac{x + ut}{2 \sqrt{(D_{bw} + D_s) t}} \right) \right)$$

(23)

where $C_0$ is the tracer concentration at the sediment surface (Bear and Verruijt, 1987). From Eq. 23 two hypothetical profiles were calculated, one where advection was neglected and one where advection was included with a downward directed velocity of 5 cm day$^{-1}$ (Fig. 4A). Both profiles are valid for a time of 1 day after the water column concentration was increased and based on identical values of $D_s$ and $D_{bw}$ of $5 \times 10^{-6}$ cm$^2$ s$^{-1}$. Each of the profiles were simulated repeatedly over a range of $N$ and time steps ($\Delta t$). The error of the numerical solution was determined as the maximum deviation in the 0 to 10 cm depth interval from the analytical solution is a percent of the concentration on the sediment surface (Figs. 4B and 4C). The error of the numerical solution decreases as expected with increasing $N$ and $\Delta t$. As a result of numerical diffusion (i.e. Patankar, 1980) the error is approximately 10-fold larger for the profile influenced by advection. This example shows that transient simulations of advection-dominated systems demands relatively high numbers of control volumes to obtain an accurate numerical solution.

d. **Example 4**

As a more realistic example from a modeling point of view, the numerical solution was implemented in a simplified version of the dynamic diagenetic model put forward by Soetaert et al., (1996). The simplification consists of neglecting the nitrogen cycling. This leaves three reactions to be simulated (Table 2), oxic mineralization, anoxic mineralization, and oxidation of so-called reduced compounds, such as $\text{NH}_4^+, \text{Mn}^{2+}, \text{Fe}^{2+}$, and $\text{H}_2\text{S}$,
which was modeled as one component and referred to as ODU (Oxygen Demanding Units). In addition to ODU, the model included O$_2$ plus a rapidly and a slowly decomposing pool of organic matter (OM). Furthermore, the active transport processes accounted for were molecular diffusion, bioturbation and burial as in the original model (Soetaert et al., 1996). The regulation of all reactions was adopted from Berg et al., (2003) (Table 2). The model was applied to the Arctic sediment of one of the sites in Young Sound, Greenland, monitored intensively by Rysgaard and Berg (1996) and Rysgaard et al., (1998) through a full annual cycle. The site is located at 36 m depth, has a constant temperature year round, and a supply of OM that follows a dynamic pattern strongly affected by a short ice-free period in mid-summer.

As a realistic test example of the numerical solution, the model contains several rather challenging elements. For example, the reaction regulations are all clearly nonlinear and result in nonlinear production terms (Table 2). These production terms couple the mass conservation equations for the four simulated components, making all four equations nonlinear. In addition, both the depth and temporal scales of these components are markedly different. Specifically, O$_2$ penetrates only a few mm into the sediment and adjusts to dynamic changes on a time scale of 10 to 100 min, while decomposing OM reaches much larger sediment depths and adjusts to changes on a time scale of 10 to 100 years.

The numerical solution was implemented as follows. As an initial step, coefficients in the systems of equations, one system for each simulated component, were evaluated and the systems of equations were decomposed by the algorithm CONSTANTS, utilized only...
once for each component. In each of the following time steps, first the reaction rates \( V_{1f}, V_{1s}, V_{2f}, V_{2s}, V_3 \) and then the production terms \( R_{OMf}, R_{OMs}, R_{O2}, R_{ODU} \) were determined from known concentrations at time \( t \) (Table 2). Based on these production terms, new concentrations for time \( t + \Delta t \) were determined by the algorithm CNEW, utilized once for each component in every time step.

This scheme relies on an explicit coupling between the mass balances through the production terms \( R_{OMf}, R_{OMs}, R_{O2}, R_{ODU} \). In order to avoid instabilities arising from this explicit coupling, especially in the initial phase of a simulation, none of the reaction rates were allowed to be negative. This was achieved by applying the intrinsic function \( \text{MAX}(a, b) \) which returns the maximum value of arguments \( a \) and \( b \).

Site-specific quantities measured by Rysgaard and Berg (1996), Rysgaard et al. (1998)
and Berg et al. (2001) were used for many input parameters to the model (1, 2, 3, 6, 7, 8, 9, 10, 11, Table 3). The limiting O₂ concentration (12, Table 3) used in the regulation of the reactions was taken from Van Cappellen and Wang (1996) and Berg et al. (2003) as was the rate constant for Reaction 3 (15, Table 3). This rate constant was used in these studies for the reaction of Fe²⁺/H₂O₂ with O₂ and by adopting this constant here, it was implicitly assumed that the ODU pool consists mostly of Fe²⁺/H₂O₂ in accordance with the findings of Berg et al. (2003) at this site. The distribution of the OM supply between the rapidly and the slowly decomposing OM pools (16, Table 3) was taken from Soetaert et al. (1996). All these parameters were kept constant in all simulations.

The last three input parameters to be assigned, the rate constants for the two OM pools and the time dependant OM flux supplied to the sediment, were given values by comparing simulated and measured results repetitively and adjusting the three input parameters. Based on the measured pattern of O₂ fluxes (Fig. 5B) and also two OM sedimentation rates (Fig. 5A) reported by Rysgaard et al. (1998), it was assumed that the variation of the OM flux over the year consists of a base contribution plus a short peak summer contribution with a duration of 1 month (Fig. 5A). With a known annual supply of OM to the sediment (9, Table 3) also reported by Rysgaard et al. (1998), the dynamic OM flux was uniquely defined by the ratio between the peak summer contribution and the base contribution (17, Table 3).

Despite the simplicity of the model, a good agreement was achieved for the O₂ uptake

Table 3. Input parameters in Example 4 and their origin.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Sedimentation rate</td>
<td>( w = 0.12 \text{ cm year}^{-1} )</td>
<td>1, 2</td>
</tr>
<tr>
<td>2 Biodiffusivity for solutes</td>
<td>( x \leq 4 \text{ cm: } D_{bw} = 4.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} )</td>
<td>3, (2)</td>
</tr>
<tr>
<td></td>
<td>( x &gt; 4 \text{ cm: } D_{bw} = 4.6 \times 10^{-6} e^{-0.35(x-4)} \text{ cm}^2 \text{ s}^{-1} )</td>
<td></td>
</tr>
<tr>
<td>3 Biodiffusivity for solids</td>
<td>( D_{bs} = D_{bw}/12 )</td>
<td>3, (2)</td>
</tr>
<tr>
<td>4 Molecular diffusivity at 0 °C</td>
<td>( D_{O2} = 11.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} )</td>
<td>4</td>
</tr>
<tr>
<td>5 Molecular diffusivity at 0 °C</td>
<td>( D_{ODU} = 3.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} )</td>
<td>5</td>
</tr>
<tr>
<td>6 Porosity</td>
<td>( \varphi = 0.631 + 0.207 e^{-1.02x} )</td>
<td>6, (2)</td>
</tr>
<tr>
<td>7 Density of solid sediment</td>
<td>( \rho_s = 2.41 \text{ g cm}^{-3} )</td>
<td>6</td>
</tr>
<tr>
<td>8 Diffusive boundary layer</td>
<td>( \delta_D = 0.03 \text{ cm} )</td>
<td>6, (2)</td>
</tr>
<tr>
<td>9 Boundary condition</td>
<td>( F_{OM} = 2300 \text{ mmol m}^{-2} \text{ year}^{-1} )</td>
<td>6</td>
</tr>
<tr>
<td>10 Boundary condition</td>
<td>( [O_2]_{lim} = 20 \text{ µM} )</td>
<td>7, (2)</td>
</tr>
<tr>
<td>11 Boundary condition</td>
<td>( [ODU]_{lim} = 389 \text{ µM} )</td>
<td>6</td>
</tr>
<tr>
<td>12 Limiting concentration.</td>
<td>( [O_2]_{lim} = 389 \text{ µM} )</td>
<td>6, (2)</td>
</tr>
<tr>
<td>13 Rate constant</td>
<td>( K_{OMf} = 2.0 \times 10^{-6} \text{ s}^{-1} )</td>
<td>*</td>
</tr>
<tr>
<td>14 Rate constant</td>
<td>( K_{OMs} = 3.0 \times 10^{-9} \text{ s}^{-1} )</td>
<td>*</td>
</tr>
<tr>
<td>15 Rate constant</td>
<td>( K_3 = 1.1 \times 10^{-6} \text{ µM}^{-1} \text{ s}^{-1} )</td>
<td>7, (2)</td>
</tr>
<tr>
<td>16 Ratio</td>
<td>( F_{OM}/F_{OMs} = 0.5 )</td>
<td>8</td>
</tr>
<tr>
<td>17 Ratio</td>
<td>( F_{OM peak}/F_{OM base} = 6 )</td>
<td>*</td>
</tr>
</tbody>
</table>

1) Rysgaard et al. (1996); 2) Berg et al. (2003); 3) Berg et al. (2001); 4) Broecker and Peng (1974); 5) Li and Gregory (1974); 6) Rysgaard et al. (1998); 7) Van Cappellen and Wang (1996); 8) Soetaert et al. (1996); *This study.
throughout the year (Fig. 5B). A similarly good agreement was obtained with the measured O$_2$ concentration profile determined by Rysgaard et al., (1998) in mid August (Fig. 5C).

All simulations were based on a time step of 1 hour and a separation of the diffusive boundary layer and the upper 20 cm of the sediment into 100 control volumes. This depth was required to diminish the slow pool of OM to close to zero concentrations (Fig. 5D). The upper 1 cm of the sediment was separated into equally sized control volumes of 0.03 cm after which the control volume size was gradually increased with depth. This discretization in time and space was found to be adequate to obtain precise numerical solutions in an additional simulation performed with a time step of 15 min and 200 control volumes which gave the same annual O$_2$ uptake within 0.04%.

From initial conditions of zero OM, O$_2$, and ODU in the sediment, 75 years of simulated
time were required to build up the OM pools to quasi-stationary conditions on a year to year basis (Fig. 5E). Even though some 50 simulations were performed in this model parameterization, the 75 years of simulated time did not lead to prohibitive computation times as the model was running at the speed of 0.13 s per simulated year on a 2.0 GHz Pentium M PC (Fig. 5F). This good performance was the combined result of three factors. Firstly, the implicit formulation in the numerical solution allowed a relatively large time step to be used. Specifically, the time step was 100 times larger than the maximum allowed critical time step of explicit formulations (see above). Secondly, the separation of the forward and the back substitution in the numerical solution allowed the system of 100 equations per simulated component to be decomposed only once, after which new concentrations were found with little computational effort in every time step. Thirdly, the novel implementation of boundary conditions allowed the values of boundary conditions to vary as simulations progressed without requiring new decompositions of the systems of equations. This characteristic was clearly taken advantage of here with respect to the imposed OM flux (Fig. 5A). An additional simulation, performed with the standard Thomas algorithm as equation solver (Eqs. 12 and 13) instead of our algorithms (Eqs. 14 and 15), required the double amount of computation time (Fig. 5F). It should be emphasized that this simulation with the standard Thomas algorithm also was optimized with respect to computation time by only calculating the constants $AA_j$, $BB_j$ and $CC_j$ (Eq. 9) once. Because the number of numeric operations in multi-component diagenetic models typically varies linearly with the number of species accounted for, this factor of two conservatively represents the computational efficiency to be gained over the Thomas algorithm by using the algorithms proposed in this study.

The explicit coupling used between the mass balances for each component represents the simplest possible way to overcome the inherent nonlinearities in multi-component diagenetic models. A more advanced implicit coupling that would allow markedly larger time steps than used here is also possible. Although this would require iterations to be performed in every time step to overcome these nonlinearities, it would lead to even faster overall computation times. In such formulations, the algorithms CONSTANTS and CNEW can also be used equally as effectively. Details on how to formulate such iterative schemes most effectively are for example given by Patankar (1980) and Berg (1999).

4. Summary and conclusion

Many researchers modeling species transformations in aquatic sediments have found that computation times of numerical solutions can become prohibitively long. In many cases, this is either due to inefficient algorithms or to algorithms being misapplied to problems inappropriate to them. The numerical solution presented here is suited to both single and multi-component models, and aims to minimize this problem, taking advantage of three factors:

1. The numerical solution is based on an implicit formulation of the discretization equation which provides a versatile approach for solving transient problems using
relatively large time steps, and at the same time, allowing steady-state solutions to linear problems to be produced in one single “infinitely large” time step.

2. Care has been taken to re-calculate model variables only when necessary, i.e., as a simulation progresses when or if they change. For example, in transient solutions all non-essential numerical operations are eliminated from the repetitive time loop. Consequently, the numerical solution consists of two algorithms, CONSTANTS and CNEW, one that decomposes the discretization matrix once and one that subsequently can be utilized numerous times with minimal computational effort. In transient solutions, this will be in every time step.

3. The algorithms are uniquely formulated to allow the values of boundary conditions to vary as a simulation progresses without requiring new decompositions of the discretization matrix.

The combined effect of these features can reduce computation times significantly relative to procedures commonly used for modeling species transformations in aquatic sediments. Although the last example presented above focuses on a relatively simple diagenetic model, it illustrates clearly the potential benefits in terms of computation times that can be achieved with this numerical solution.

Available Software

Copies of the algorithms CONSTANTS and CNEW, coded in FORTRAN 90, can be obtained free of charge from the corresponding author. For optimal performance, the algorithms should be applied in double precision.

Acknowledgments. We thank D. Burdige and one anonymous reviewer for their constructive reviews of this paper. This study was supported by grants from the University of Virginia and the Danish National Science Research Councils (contract nos. 9501025 and 9700224).

APPENDIX A

Approximation of fluxes

As illustrated by Patankar (1980) a first evaluation of flux-approximating schemes can be achieved by comparison with the analytical solution of the one-dimensional steady state mass-conservation equation that accounts for diffusion and advection. This approach is adapted here, and complemented with computation times for evaluation of the schemes on modern computer processors. The one-dimensional steady state mass-conservation equation including diffusive and advective transport contributions can be written in the form

\[ \frac{dJ}{dx} = 0 \]

\[ J = -H_2 \frac{dC}{dx} + H_3 C \]
If $H_2$ and $H_3$ are constant with depth, Eq. A1 have the analytical solution (i.e. Patankar, 1980 or Boudreau, 1997)

\[ \begin{align*}
  x = 0: & \quad C = C_0 \\
  x = L: & \quad C = C_L
\end{align*} \]

\[ J = H_3 \left( C_0 + \frac{C_0 - C_L}{\exp \left( \frac{H_3}{H_2} L \right) - 1} \right) \]  \hspace{1cm} (A2)

Assuming for now that $\Delta x_j$ is constant with depth and referred to as $\Delta x$, and using this solution to express the intermediate combined diffusive-advective flux, $J_{j-1/2}$, at the boundary between control volume $j-1$ and $j$, gives

\[ J_{j-1/2} = H_3 \left( C_{j-1} + F(P) \frac{C_{j-1} - C_j}{P} \right) \]  \hspace{1cm} (A3)

where the function $F(P)$ is given by

\[ F(P) = \frac{P}{\exp(P) - 1} \]  \hspace{1cm} (A4)

and where $P$ is the Peclet number defined as

\[ P = \frac{H_3}{H_2} \Delta x \]  \hspace{1cm} (A5)

Numerical solutions of Eq. 1 can be produced by expressing the fluxes between control volumes according to Eq. A3. The expression of $J_{j-1/2}$ in combination with Eq. A4 is often referred to as the exponential scheme based on the expression for $F(P)$ and was first put forward by Spalding (1972) and later by Fiadeiro and Veronis (1977). At the time when the exponential scheme was defined, the exponential function was time consuming to evaluate on computers of the day. In addition, $F(P)$ needs special attention in its evaluation as it contains a singularity for $P = 0$. For those reasons, researchers derived new schemes relying on approximations of $F(P)$ that were markedly faster to evaluate (i.e. Spalding, 1972; Patankar, 1981; Berg, 1985). The most popular schemes, including the classic central difference and upwind schemes (Courant et al., 1952), are shown in Table A1 along with the normalized computation time for their evaluation on a 2.0 GHz Pentium M PC. As an example of derivation, the central difference approximation of $F(P)$ can be derived by approximating the intermediate flux as $J_{j-1/2} = -H_2(C_j - C_{j-1})/\Delta x + H_3(C_j + C_{j-1})/2$ which is equivalent to Eq. A3 if $F(P) = 1 - 0.5P$ (Table A1). The exact function $F(P)$ and its approximations are illustrated in Figure A1.

The central difference scheme provides a good approximation of $F(P)$ only for small values of $P$, and is the only scheme in which the divergence from $F(P) \to \infty$ as $P \to \pm \infty$ (Fig. 1A). This characteristic explains why instabilities occur when using central difference approximation for advection-dominated systems ($|P| \gg 0$). The normalized computation times (Table A1) show that the power law scheme which was used extensively in the 1980s and 1990s, is outdated today as its evaluation is more time consuming.
than the exact scheme. Both the hyperbolic and the hybrid scheme appear to be good choices based on their good approximation of $F(P)$ (Fig. A1) in combination with their relatively short evaluation times. However, it should be noted that the evaluation time

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Approximations of $F(P) = P/(\exp(P) - 1)$</th>
<th>Normalized time for one evaluation</th>
<th>Reference</th>
</tr>
</thead>
</table>
| Exact    | $P_{help} = \text{SIGN} (\text{MAX}(10^{-5}, |P|), P)$  
$F(P) = P_{help}/(\exp(P_{help}) - 1)$ | 1.0 1), 2)                     |           |
| Power law| $F(P) = \text{MAX}(0, (1 - 0.1|P|)^5) + \text{MAX}(0, -P)$                           | 1.2 3)                           |           |
| Hyperbolic| $F(P) = \text{MAX}(0, 8/(4 + |P| - 1) + \text{MAX}(0, -P)$                           | 0.093 4)                         |           |
| Hybrid   | $F(P) = \text{MAX}(0, -P, 1 - 0.5P)$                                                                                   | 0.062 1)                         |           |
| Upwind   | $F(P) = \text{MAX}(1, 1 - P)$                                                                                         | 0.047 5)                         |           |
| Central  | $F(P) = 1 - 0.5P$                                                                                                      | 0.037                             |           |


Figure A1. The exact function $F(P)$ and its approximation in alternate schemes.
should affect the choice of scheme only in model formulations where numerous evaluations of $F(P)$ are expected.

In this brief comparison it was assumed that $\Delta x$, $H_2$, and $H_3$ are constant with depth. This is only true for $H_3$ in Eq. 3, and an expression similar to Eq. A3 where variations in $\Delta x$ and $H_2$ are accounted for is derived from Eq. A2 as follows. Assuming that the grid point values of $H_3$ prevail throughout control volumes as representative mean values, the flux $J_{j-1/2}$ can be expressed for control volume $j-1$ by the variables $C_{j-1}$, $C_{j-1/2}$, $\Delta x_{j-1}$, $H_{2j-1}$, and $H_3$ as

$$J_{j-1/2} = H_3 \left( C_{j-1} + \frac{C_{j-1} - C_{j-1/2}}{\exp \left( \frac{H_3}{H_{2j-1}} \frac{1}{2} \Delta x_{j-1} \right) - 1} \right) \tag{A6}$$

The same flux can similarly be expressed for control volume $j$ by the variables $C_{j-1/2}$, $C_j$, $\Delta x_j$, $H_{2j}$, and $H_3$ as

$$J_{j-1/2} = H_3 \left( C_{j-1/2} + \frac{C_{j-1/2} - C_j}{\exp \left( \frac{H_3}{H_{2j}} \frac{1}{2} \Delta x_j \right) - 1} \right) \tag{A7}$$

Eliminating $C_{j-1/2}$ by combining these two expressions leads to (equivalent to Eq. A3)

$$J_{j-1/2} = H_3 \left( C_{j-1} + F(P_{j-1/2}) \frac{C_{j-1} - C_j}{P_{j-1/2}} \right) \tag{A8}$$

where the function $F(P_{j-1/2})$ is given by (equivalent to Eq. A4)

$$F(P_{j-1/2}) = \frac{P_{j-1/2}}{\exp(P_{j-1/2}) - 1} \tag{A9}$$

and the Peclet number $P_{j-1/2}$ is defined as the simple average of $P_{j-1}$ and $P_j$ (equivalent to Eq. A5)

$$P_{j-1/2} = \frac{1}{2} \left( \frac{H_3 \Delta x_{j-1}}{H_{2j-1}} + \frac{H_3 \Delta x_j}{H_{2j}} \right) \tag{A10}$$

or alternatively as

$$P_{j-1/2} = \frac{H_3}{H_{2j-1/2}} \frac{1}{2} (\Delta x_{j-1} + \Delta x_j) \tag{A11}$$

where $H_{2j-1/2}$ is given by the weighted harmonic mean of $H_{2j-1}$ and $H_{2j}$ as

$$H_{2j-1/2} = \frac{H_{2j-1} H_{2j} (\Delta x_{j-1} + \Delta x_j)}{\Delta x_{j-1} H_2 + \Delta x_j H_{2j-1}} \tag{A12}$$
The general expression of the flux $J_{j-1/2}$ over the boundary between control volume $j-1$ and $j$ is defined by the two variables, $F_{1j}$ and $F_{2j}$, (Eq. 5). These variables can now be derived from Eq. A8 as

$$F_{1j} = -F(P_{j-1/2}) \frac{H_{2j-1/2}}{\frac{1}{2}(\Delta x_{j-1} + \Delta x_j)}$$

$$F_{2j} = -F_{1j} + H_3$$

where the function $F(P_{j-1/2})$ is taken from Table A1.

**APPENDIX B**

The algorithm "CONSTANTS"

Below is listed the input to and the output from the algorithm CONSTANTS, followed by a summary of the algorithm. Units of input and output variables are included as an example. Other units can be used as long as they are mutually consistent.

**Input:**
- $L$ [-] Number of first control volume (=1 or $M$, see Fig. 1)
- $M$ [-] Number of control volume at the sediment surface (see Fig. 1)
- $N$ [-] Number of last control volume (see Fig. 1)
- $\Delta t$ [s] Time step
- $\Delta x_j$ [cm] Size of control volumes
- $\varphi_j$ [-] Porosity
- $D_j$ [cm$^2$ s$^{-1}$] Diffusivity in water
- $D_{Bw,j}$ [cm$^2$ s$^{-1}$] Biodiffusivity for solutes
- $D_{Bs,j}$ [cm$^2$ s$^{-1}$] Biodiffusivity for solids
- $\rho_s$ [g cm$^{-3}$] Density of sediment
- $\alpha_j$ [s$^{-1}$] Irrigation coefficient
- $R_{2j}$ [s$^{-1}$] Production rates
- $(\varphi u)_x$ [m s$^{-1}$] Porosity times porewater velocity (constant with depth)
- $((1 - \varphi) w)_x$ [m s$^{-1}$] One minus porosity times burial velocity (constant with depth)
- $\xi$ [-] Equal to 1 for solutes and equal to 0 for solids
- $\kappa$ [cm$^3$ g$^{-1}$] Coefficient (=0, 1 or $K'$ where $K'$ is the adsorption constant)
- $FL_0$ [-] Flag for choosing the expression for $D_j$ (=1, 2, 3, 4 or 5)
- $FL_1$ [-] Flag for choosing the upper boundary condition (=1, 2, or 3)
- $FL_2$ [-] Flag for choosing the lower boundary condition (=1, 2, or 3)

**Output:**
- $AA_j$ [cm s$^{-1}$] Input to CNEW
- $EE_j$ [cm s$^{-1}$] Input to CNEW
- $FF_j$ [cm s$^{-1}$] Input to CNEW
- $NN_j$ [s cm$^{-1}$] Input to CNEW
- $PP_j$ [-] Input to CNEW
- $F_{1j}$ [cm s$^{-1}$] Constants for calculation of flux (Eq. 5)
- $F_{2j}$ [cm s$^{-1}$] Constants for calculation of flux (Eq. 5)

Calculation of $D_{sj}$ depending of the flag $FL_0$: 

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Calculation of \( H_{1j}, H_{2j}, H_3, \) and \( H_{4j}: \)

\[
\begin{align*}
H_3 &= \xi(\varphi u)_x + \rho_s(1 - \varphi) w_N \kappa \\
H_{1j} &= \xi \varphi_j + \rho_s(1 - \varphi_j) \kappa \\
H_{2j} &= \xi \varphi_j(D_{bwj} + D_{sj}) + \rho_s(1 - \varphi_j) D_{bsj} \kappa \\
H_{4j} &= \xi \varphi_j \alpha_j
\end{align*}
\]  

(B2) \( j = L \rightarrow N \)

Calculation of \( F_{1j} \) and \( F_{2j}. \) Note that special precautions are taken to avoid division by zero. The function MAX\((a, b)\) is a standard function in FORTRAN and returns the maximum value in the argument list. The number \( 10^{-36} \) is close to the smallest value that can be represented in single precision in FORTRAN.

\[
\begin{align*}
H_{2j-1/2} &= \frac{H_{2j-1} H_2 j \left( \Delta x_{j-1} + \Delta x_j \right)}{\text{MAX}(10^{-36}, \Delta x_{j-1} H_{2j} + \Delta x_j H_{2j-1})} \\
P_{j-1/2} &= \frac{H_3}{\text{MAX}(10^{-36}, H_{2j-1/2})} \left( \Delta x_{j-1} + \Delta x_j \right) \\
F(P_{j-1/2}) &= \text{MAX}(0, 8(4 + |P_{j-1/2}|) - 1) + \text{MAX}(0, -P_{j-1/2}) \\
F_{1j} &= -F(P_{j-1/2}) \frac{H_{2j-1/2}}{\frac{1}{2} \left( \Delta x_{j-1} + \Delta x_j \right)} \\
F_{2j} &= -F_{1j} + H_3
\end{align*}
\]  

(B3) \( j = L + 1 \rightarrow N \)

Calculation of the coefficients \( AA_j, BB_j \) and \( CC_j \) in the tri-diagonal system of equations:

\[
\begin{align*}
AA_j &= F_{2j} \\
BB_j &= F_{1j} - F_{2j+1} - H_{4j} \Delta x_j + R_{2j} \Delta x_j - H_{1j} \frac{\Delta x_j}{\Delta l} \\
CC_j &= -F_{1j+1}
\end{align*}
\]  

(B4) \( j = L + 1 \rightarrow N - 1 \)

Calculation of the coefficients \( BB_L \) and \( CC_L \) for the upper boundary condition. The type of boundary condition is specified by the flag \( FL_1: \)
Calculation of the coefficients $AA_N$ and $BB_N$ for the lower boundary condition. The type of boundary condition is specified by the flag $FL_2$:

$FL_2 = 1$: $AA_N = 0$; $BB_N = 1$

$FL_2 = 2$: $AA_N = F_{2N}$; $BB_N = F_{1N}$

$FL_2 = 3$: $AA_N = -\frac{2}{\Delta x_{N-1}}$; $BB_N = -AA_N$ (B6)

Calculation of the coefficients $NN_j$ and $PP_j$ in the forward substitution:

$$NN_L = \frac{1}{BB_L}; \quad PP_L = -CC_LNN_L$$

$$NN_j = \frac{1}{BB_j + AA_jPP_{j-1}} \left( j = L + 1 \rightarrow N - 1 \right)$$

$$PP_j = -CC_jNN_j$$

$$NN_N = \frac{1}{BB_N + AA_NPP_{N-1}}$$

Calculation of the coefficients $EE_j$ and $FF_j$ used to calculate the right hand side in the tri-diagonal system of equations:

$$EE_j = H_{1j} \frac{\Delta x_j}{\Delta t}$$

$$FF_j = H_{4j} \Delta x_j \left( j = L + 1 \rightarrow N - 1 \right)$$

**APPENDIX C**

The algorithm “CNEW”

Below is listed the input to and the output from the algorithm CNEW, followed by a summary of the algorithm. Units of input and output variables are included as an example. Other units can be used as long as they are mutually consistent.

Input:

- $L$ [-] Number of first control volume (=1 or $M$, see Fig. 1)
- $N$ [-] Number of last control volume (see Fig. 1)
- $\Delta x_j$ [cm] Size of control volumes
- $AA_j$ [cm s$^{-1}$] Input from CONSTANTS
- $EE_j$ [cm s$^{-1}$] Input from CONSTANTS
- $FF_j$ [cm s$^{-1}$] Input from CONSTANTS
Input (continued):

- \( N N_j \) [s cm\(^{-1}\)] Input from CONSTANTS
- \( PP_j \) [-] Input from CONSTANTS
- \( C_0 \) [nmol cm\(^{-3}\)] Known water column concentration
- \( C_j^n \) Solute: [nmol cm\(^{-3}\)] Known concentrations at the old time level
  Solid: [nmol g\(^{-1}\)]
- \( R_{1,j} \) [nmol cm\(^{-3}\) s\(^{-1}\)] Production rates
- \( BC_L \) Known boundary condition at top
  \( FL_1 = 1: \) [nmol cm\(^{-3}\)] or [nmol g\(^{-1}\)]
  \( FL_1 = 2: \) [nmol cm\(^{-2}\) s\(^{-1}\)]
  \( FL_1 = 3: \) [nmol cm\(^{-4}\)] or [nmol g\(^{-1}\) cm\(^{-1}\)]
- \( BC_N \) Known boundary condition at bottom
  \( FL_2 = 1: \) [nmol cm\(^{-3}\)] or [nmol g\(^{-1}\)]
  \( FL_2 = 2: \) [nmol cm\(^{-2}\) s\(^{-1}\)]
  \( FL_2 = 3: \) [nmol cm\(^{-4}\)] or [nmol g\(^{-1}\) cm\(^{-1}\)]

Output:

- \( C_j^{n+1} \) Solute: [nmol cm\(^{-3}\)] New concentrations at the new time level
  Solid: [nmol g\(^{-1}\)]

Calculation of the coefficients \( QQ_j \):

\[
QQ_L = BC_L N N_L
\]

\[
QQ_j = ( - EE_j C_j^n - FF_j C_0 - R_{1,j} \Delta x_j - AA_j QQ_{j-1} ) N N_j \quad (j = L + 1 \rightarrow N - 1) \quad (C1)
\]

Calculation of the new concentrations \( C_j^{n+1} \):

\[
C_j^{n+1} = (BC_N - AA_N QQ_{N-1}) N N_N
\]

\[
C_j^{n+1} = PP_j C_j^{n+1} + QQ_j \quad (j = N - 1 \rightarrow L) \quad (C2)
\]

REFERENCES


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