Chapter 1

Solute movement

1.1 Advection-dispersion equation

For describing the solute movement, the soil matrix water is divided into two parts, a mobile and an immobile part

$$\theta = \theta_m + \theta_{im} \tag{1.1}$$

where θ_m and θ_{im} are the mobile and immobile water content, respectively. The immobile part of θ is always filled first. Reversely is the mobile part emptied first. Thus, the immobile part of θ can be expressed as

$$\theta_{im} = \begin{cases} \theta & \text{for } \theta < \theta_{im,max} \\ \theta_{im,max} & \text{for } \theta \geq \theta_{im,max} \end{cases} \tag{1.2}$$

where the mobile part of θ can then expressed as

$$\theta_m = \begin{cases} 0 & \text{for } \theta < \theta_{im,max} \\ \theta - \theta_{im,max} & \text{for } \theta \geq \theta_{im,max} \end{cases} \tag{1.3}$$

The solute concentration is similarly divided into a part associated with the immobile water, C_{im} and a part associated with the mobile water, C_m. Dividing the matrix water content into a mobile and an immobile volume is somewhat inconsistent when $\theta_{im,max} > \theta_r$ where θ_r is the residual water content. When comparing to Richards' equation all water above θ_r is subject to movement. From Richards' equation the Darcy velocity can be calculated as $\mathbf{v} = \mathbf{q}/\theta$. The flux, $\mathbf{q}$ as used for calculating the movement of solute in the mobile volume is calculated as

$$\mathbf{q}_m = \begin{cases} \mathbf{0} & \text{for } \theta_m = 0 \\ \mathbf{q} & \text{for } \theta_m > 0 \end{cases} \tag{1.4}$$

where the associated flow velocity is given as

$$\mathbf{v}_m = \mathbf{q}_m / \theta_m \tag{1.5}$$

Three physical processes can contribute to movement of solutes in the matrix part (non macroporous part) of soil:

- advection

- molecular diffusion

- hydrodynamic dispersion (only in connection with advection)

Advection (or bulk flow) is the process where the dissolved chemical moves with the soil solution. The flux of solute can be described as:

$$\mathbf{j} = \mathbf{q}_m C_m \tag{1.6}$$

The Molecular diffusion is a result of the Brownian motion (random walk) of the molecules. A process related to the movement of the water is the hydrodynamic dispersion, which is a consequence of the fact that flow is not uniform, because the flow paths move around obstacles and air, but also because of variation in pore size and the nonuniform velocity distribution inside the pores. Mathematically the hydrodynamical dispersion process can be described as a diffusion process. The movement by diffusion like processes can be expressed as:

$$\mathbf{j} = -\theta_m \mathbf{D} \nabla C_m, \quad \mathbf{D} = \begin{bmatrix} D_{xx} & D_{xz} \\ D_{zx} & D_{zz} \end{bmatrix} \tag{1.7}$$

where $\mathbf{D}$ is the dispersion tensor (or matrix). The consequence is that the solute tries to move from areas with high concentration to areas with lower concentration. The elements in $\mathbf{D}$ are often calculated as:

$$
\begin{aligned}
D_{xx} &= \alpha_L \frac{v_{m,x}^2}{|\mathbf{v}_m|} + \alpha_T \frac{v_{m,z}^2}{|\mathbf{v}_m|} + D^* \\
D_{zz} &= \alpha_L \frac{v_{m,z}^2}{|\mathbf{v}_m|} + \alpha_T \frac{v_{m,x}^2}{|\mathbf{v}_m|} + D^* \\
D_{xz} &= D_{zx} = (\alpha_L - \alpha_T) \frac{v_{m,x} v_{m,z}}{|\mathbf{v}_m|}
\end{aligned}
\tag{1.8}
$$

where D^* is the molecular diffusion. The rest of the terms are arising from the hydrodynamic dispersion. α_L is called the longitudinal dispersion and α_T the transversal dispersion. The molecular diffusion can be calculated as:

$$D^* = \tau D_0 \tag{1.9}$$

where D_0 is the diffusion coefficient for the solute in free water and τ is the tortuosity factor. As an example ?) sugested:

$$\tau = \frac{\theta_m^{7/3}}{\theta_s} \tag{1.10}$$

If we are using equation (1.10) and expressing the mean velocity in the pores associated with solute movement by $\mathbf{q}_m$ and θ_m, the elements of $\theta_m\mathbf{D}$ can be expressed as:

$$\theta_m D_{xx} = \alpha_L \frac{q_{m,x}^2}{|\mathbf{q}_m|} + \alpha_T \frac{q_{m,z}^2}{|\mathbf{q}_m|} + D_0 \frac{\theta_m^{10/3}}{\theta_s}$$

$$\theta_m D_{zz} = \alpha_L \frac{q_{m,z}^2}{|\mathbf{q}_m|} + \alpha_T \frac{q_{m,x}^2}{|\mathbf{q}_m|} + D_0 \frac{\theta_m^{10/3}}{\theta_s} \tag{1.11}$$

$$\theta_m D_{xz} = \theta_m D_{zx} = (\alpha_L - \alpha_T)\frac{q_{m,x}q_{m,z}}{|\mathbf{q}_m|}$$

The solute movement can be expressed as a sum of the advection and the diffusion process:

$$\mathbf{j}_m = \theta_m C_m \mathbf{v}_m - \theta_m \mathbf{D}\nabla C_m = C_m\mathbf{q}_m - \theta_m\mathbf{D}\nabla C_m \tag{1.12}$$

The mass balance for the solute can be expressed as:

$$\frac{\partial(\rho_b C_a)}{\partial t} + \frac{\partial(\theta_m C_m)}{\partial t} + \frac{\partial(\theta_{im} C_{im})}{\partial t} + \frac{\partial(\theta_{mp} C_{mp})}{\partial t}$$
$$= -\nabla\cdot\mathbf{j}_m - \nabla\cdot\mathbf{j}_{mp} - \Gamma \tag{1.13}$$

where ρ_b is the soil bulk density and C_a is the concentration in the adsorbed phase. θ_{mp} is the volumetric water content in the macropore domain and C_{mp} is the concentration. Γ is the sink term of the solute.

For simplification of the solute movement model, the matrix water flow and the solute movement is inside each time step considered as decoupled from the immobile water, the adsorbed phase and the macropore domain. Thus, every exchange with the environment is based on the state at start of the time step. The mass balance of dissolved solutes in the mobile matrix water yields:

$$\frac{\partial(\theta_m C_m)}{\partial t} = -\nabla\cdot\mathbf{j}_m - \Gamma_m \tag{1.14}$$

where Γ_m is the sink term which remove solutes from the mobile matrix water. The removed (or added) solute can be absorbed, moved to the immobile water or the macropore domain or be subject to chemical or biological reduction.

The boundary conditions to the equation specifies a combination of C_m and its derivative on the boundary. Also here, the *Dirichlet* boundary condition (specified concentration) and the *Neumann boundary condition*, where the flux through the boundary is specified, are common. The Dirichlet boundary condition is:

$$C_m = C_{m,0} \tag{1.15}$$

where $C_{m,0}$ is the predescribed concentration. The Neumann boundary condition is:

$$\bar{\mathbf{n}} \cdot (C_m \mathbf{q}_m - \theta_m \mathbf{D} \nabla C_m) = \bar{\mathbf{n}} \cdot \mathbf{j}_m = j_m \tag{1.16}$$

where j_m is the size of the flux, positive for outward flux. As boundary condition for the ingoing flow $j_m = \bar{\mathbf{n}} \cdot \mathbf{q}_m C_{m,0} = q_m C_{m,0}$ is often used where $C_{m,0}$ is the concentration of the flow. As lower or downstream boundary condition $j_m = \bar{\mathbf{n}} \cdot \mathbf{q}_m C_m = q_m C_m$ is often used. In both cases it is assumed that the diffusion crossing the border is zero.

Summarized, the problem to be solved for determination of the concentration of solute in Ω is:

$$\begin{cases} \theta_m \frac{\partial C_m}{\partial t} + C_m \frac{\partial \theta_m}{\partial t} = -\nabla \cdot (C_m \mathbf{q}_m - \theta_m \mathbf{D} \nabla C_m) - \Gamma_m & \text{in } \Omega \\ \bar{\mathbf{n}} \cdot (C_m \mathbf{q}_m - \theta_m \mathbf{D} \nabla C_m) = j_m & \text{on } \partial\Omega_1 \\ C_m = C_{m,0} & \text{on } \partial\Omega_2 \end{cases} \tag{1.17}$$

where $\partial\Omega_1$ is the part of the boundary with Neumann condition, and $\partial\Omega_2$ is the part of the boundary with Dirichlet boundary conditions. Also here it is not necessary that $\partial\Omega_1$ and $\partial\Omega_2$, respectively, are coherent.

1.2 Numerical solution

The basic principles behind the finite volume modeling of the solute transport is very similar to the numerical solution of the water movement equation (Richards' equation). But there are some differences. One of the major differences is that the advection diffusion equation is considered as linear inside each timestep. I.e. coefficients in the equation in each timestep is independent of the concentrations in the current timestep. This simplification can be done when the size of the sources are dependent only on the concentrations in the previous timstep. Similar are adsorption added as sink/source term. Thus different from the water movement simulation, the Picard iterations loop used inside each timestep can be avoided.

1.2.1 Stabilization methods

There is often a lot of numerical problems involved with the solving of the convection diffusion problem especially when the problems are dominated by convection. The numerical solutions have often unexpected oscillations in that situation. There have been developed a lot of more or less complicated methods to reduce the problems. Three of the methods are *upstream weighting*, *streamline diffusion*, and *timestep reduction*.

Upstream weighting

When steep concentration fronts occur, numerical oscillations can raise. A method to stabilize the system is to apply upstream weighting for the advective solute movement. For advective transport between two cells is the concentration at the face between the cells normally calculated as the average concentration of the two cells. For fully upstream weighting is the concentration at the cell face equal to the upstream concentration.

In Daisy2D it is possible to set a parameter, $0 \leq \alpha \leq 1$ where $\alpha = 1$ corresponds to a fully upstream weighting and $\alpha = 0.5$ corresponds to setting the cell face concentration to the average concentration of the two cells. It is not recommended to apply a $\alpha < 0.5$.

P_e and C_r numbers

There are two different numbers which are important for the stability. The *Peclet number*:

$$P_e = v\Delta x/D \qquad (1.18)$$

where v is the velocity, Δx is the space increment and D is the diffusion coefficient (including molecular diffusion and hydrodynamic dispersion). The *Courant number* is defined as:

$$C_r = v\Delta t/\Delta x \qquad (1.19)$$

Theoretical stability investigations are rather complicated, especially in a two or three-dimensional space with heterogenous soil. Most of the theoretical stability considerations are done for one-dimensional flow with uniform velocity. The classical constraints for stability for the standard Crank-Nicholson-Galerkin (Finite Element Method) is $P_e \leq 2$ and $C_r \leq 1$, **?**).

It can easily be concluded that keeping the Courant number lower than one is just a question of sufficiently small timesteps. But is it possible to make a mesh which under all circumstances prevents that the Peclet number raises over 2?. The peclet number for the flow in the x-direction is:

$$
\begin{aligned}
(P_e)_x &= \frac{q_x \Delta x}{\theta D_{xx}} = \frac{q_x \Delta x}{\alpha_L \frac{q_x q_x}{|\mathbf{q}|} + \alpha_T \frac{q_y q_y}{|\mathbf{q}|} + D_0 \frac{\theta^{10/3}}{\theta_s}} \\
&< \frac{q_x \Delta x}{\alpha_T \frac{q_x q_x + q_y q_y}{|\mathbf{q}|}} = \frac{q_x \Delta x}{\alpha_T |\mathbf{q}|} \leq \frac{\Delta x}{\alpha_T}
\end{aligned}
\qquad (1.20)
$$

where it is assumed that $\alpha_L \geq \alpha_T$. The same procedure can of course be used to evaluate $(P_e)_y$. It can then be concluded that the maximum Peclet number is lower than $\Delta x/\alpha_T$. If the longitudinal dispersivity is 5 cm and the transversal is 1/10 of the longitudinal and the maximum allowed P_e is 2 can it

be concluded that the maximum side length of the elements shall be approximately 1 cm. This will result in a very fine mesh.

Besides the upstream weighting method it is possible to choose between 2 stabilizing methods:

1. Introducing extra diffusion in the streamline direction so $P_e C_r \leq \gamma$. Where γ is the performance index.

2. Varying the size of Δt so $P_e C_r \leq \gamma$.

It is of course also possible to deselect any stabilizing methods. The last stabilizing method is straight forward, but the first deserves its own subsection:

Streamline diffusion

For practical situation are there often stability so long $P_e C_r \leq \gamma$ where $2 \leq \gamma \leq 10$, **?**) which under all circumstances is less restrictive than keeping both $P_e \leq 2$ and $C_r \leq 1$. γ is called the *performance index*.

In the streamline diffusion is according to **?**) added some additional longitudinal dispersion to prevent that $P_e C_r$ raises over the chosen performance index. The additional longitudinal dispersion, $\bar{\alpha}_L$ is calculated as:

$$\bar{\alpha}_L = \begin{cases} \frac{|\mathbf{v}|\Delta t}{\gamma} - \alpha_L - \frac{D^*}{|\mathbf{v}|}, & \text{for } \alpha_L + \frac{D^*}{|\mathbf{v}|} < \frac{|\mathbf{v}|\Delta t}{\gamma} \\ 0, & \text{for } \alpha_L + \frac{D^*}{|\mathbf{v}|} \geq \frac{|\mathbf{v}|\Delta t}{\gamma} \end{cases} \tag{1.21}$$

Stability tests

To investigate the stability of the numerical model is a simple system modeled. The situation here is a one-dimensional column, horizontal column with steady-state water flow with pore velocity v. And a given diffusion, D (both molecular diffusion and hydrodynamic dispersion). For the present test is the solute non-adsorping. For a scenario with linear adsorping (constant retardation factor) the adsorption have a stabilizing effect, thus for linear adsorping solutes the model is expected to be more stable. The advection-dispersion equation in one dimension can be written as:

$$\frac{\partial C_m}{\partial t} = D \frac{\partial^2 C_m}{\partial x^2} - v \frac{\partial C_m}{\partial x} \tag{1.22}$$

where $v = q\theta$. The initial condition is a zero concentration in the whole column:

$$C_m(x, 0) = 0 \tag{1.23}$$

At the left boundary is the solute flux constant.

$$\left(-D \frac{\partial C}{\partial x} + vC \right) \Big|_{x=0} = \begin{cases} vC_0, & 0 < t \leq t_0 \\ 0, & t > t_0 \end{cases} \tag{1.24}$$

The solution can then according to **?**) be written as:

For the simulations is made a water flow situation with steady state flow with the chosen pore water velocity $v = 1$ cm/hour. $C_{m,0}$ is for the simplicity chosen to 1 and $D = 0.05$ cm^2/hour. For the Daisy simulations is the virtual soil column 10 cm wide and 1 cm high. On the domain is generated a regular mesh with 100 equally large elements, each with $\Delta x = 0.1$ cm. With Δt chosen to 1 hour are $C_r = 10$ and $P_e = 2$, i.e. $P_e C_r = 20$. The numerical parameter, ω is set to $1/2$, i.e. a Crank-Nicholson scheme.

In figure 1.1 is the analytical solution compared with numerical solutions with and without upstream weighting corresponding to $\alpha = 1$ and $\alpha = 0.5$, respectively. Streamline diffusion and timestep reduction has not been applied. As it can be observed, are the wiggles significantly smaller when applying upstream weighting. The only drawback seems to be slightly more numerical diffusion compared with the numerical solution for $\alpha = 0.5$.
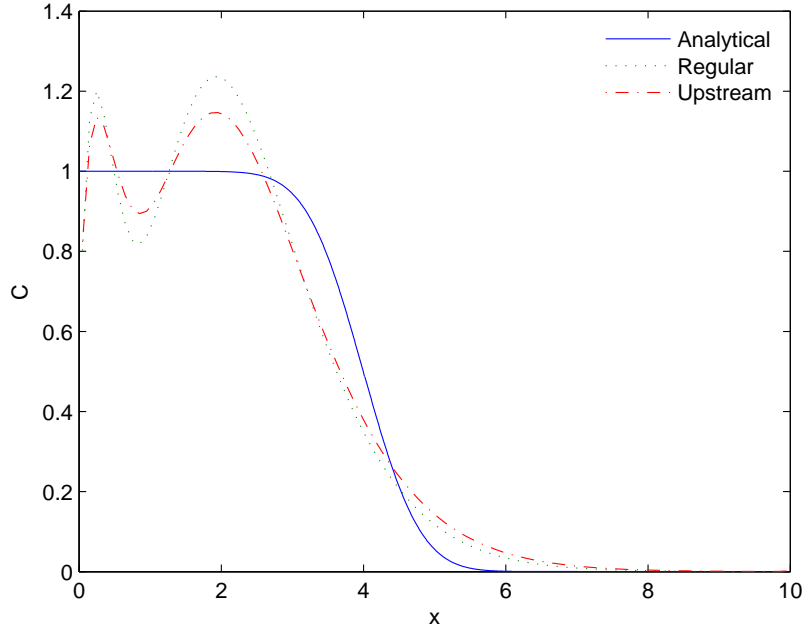

Figure 1.1: Analytical solution compared with numerical solution with regular weighting ($\alpha = 0.5$) and upstream weighting ($\alpha = 1.0$). The solutions are shown as concentration as function of x after simulation of 4 hours. For the actual case are $v = 1$ cm/hour, $D = 0.05$ cm^2/hour. For the numerical simulations are $\Delta t = 1$ hour and $\Delta x = 0.1$ cm, i.e. $P_e = 2$ and $C_r = 10$.

In the following cases upstream weighting has not been applied ($\alpha = 0.5$).

In figure 1.2 is the analytical solution shown. Besides is the numerical solution shown for the cases: no stabilization, timestep reduction and streamline diffusion. For both the timestep reduction and streamline diffusion method is the performance index, $\gamma = 10$ chosen. For the simulation without any stabilization are the wiggles significant. The wiggles are smaller for the simulation with streamline diffusion. By comparing with the analytical solution can the additional diffusion be observed. The additional diffusions effectively reduced the P_e-number from 20 to 10. The remaining graph shows the simulation with the timestep reduction stabilizing method where the size of Δt is changed so $P_e C_r \leq 10$. Here the the size of the timestep is reduced from $\Delta t = 1$ hour (no stabilization) to 0.5 hour. Effectively the C_r-number is reduced from 10 to 5, i.e. for the computation is used 2 times so many timesteps (or approximately 2 times so long CPU-time). Compared with the numerical solution without stabilization are wiggles reduced, but have also smaller wavelength.
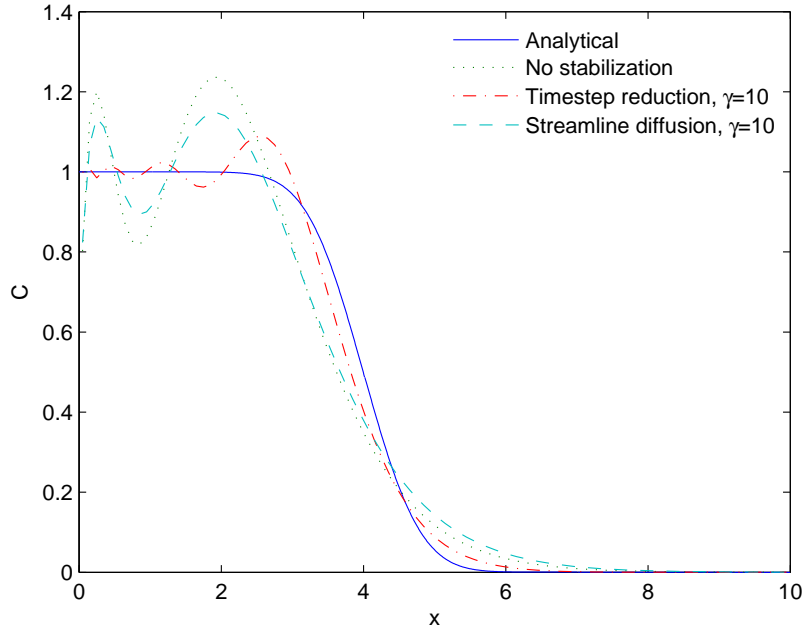

Figure 1.2: Analytical solution compared with different numerical solutions. The solutions are shown as concentration as function of x after simulation of 4 hours. For the numerical solution without stabilization are $P_e = 2$ and $C_r = 10$.

In figure 1.3 is the analytical and numerical solutions shown. The numerical

solution are computed using different performances indexes. The performance index, γ is changed applying timestep reduction. It can be observed that the wiggles are significant for $\gamma = 10$, but for $\gamma = 5$ (and lower) the size of the wiggles seems to be acceptable for most purposes.
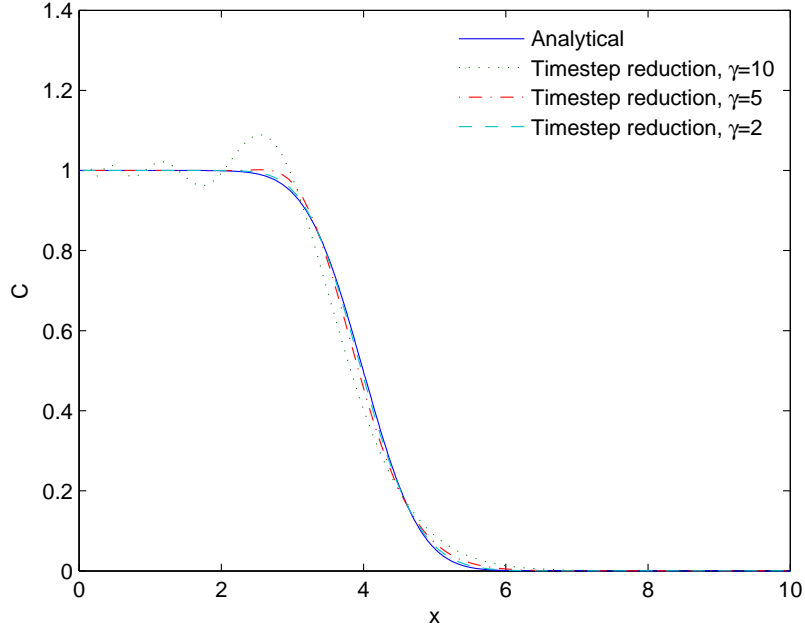

Figure 1.3: Analytical solution compared with different numerical solutions obtained using timestep reduction with varying performance index. For the simulation are $v = 1$ cm/hour and $D = 0.05$ cm^2/hour. For the numerical simulations are $\Delta x = 0.1$ cm and Δt is ranging from 1/10 hour ($\gamma = 2$) to 1/2 hour ($\gamma = 10$).

In figure 1.4 is the analytical solution shown. Also the numerical solution for varying performances indexes are shown. The performance index, γ is changed applying streamline diffusion. The wiggles are reduced when using a low value of γ, but compared with the analytical solution, the steepness of the front is reduced dramatically.

1.2.2 Upper boundary condition

The upper boundary condition describes the movement of solute applied at the surface that moves into the soil. It also describes the movement of solutes out from the domain if the water is flowing out at the upper boundary.

If the soil surface not is ponded, the flux into the soil is moved by advection
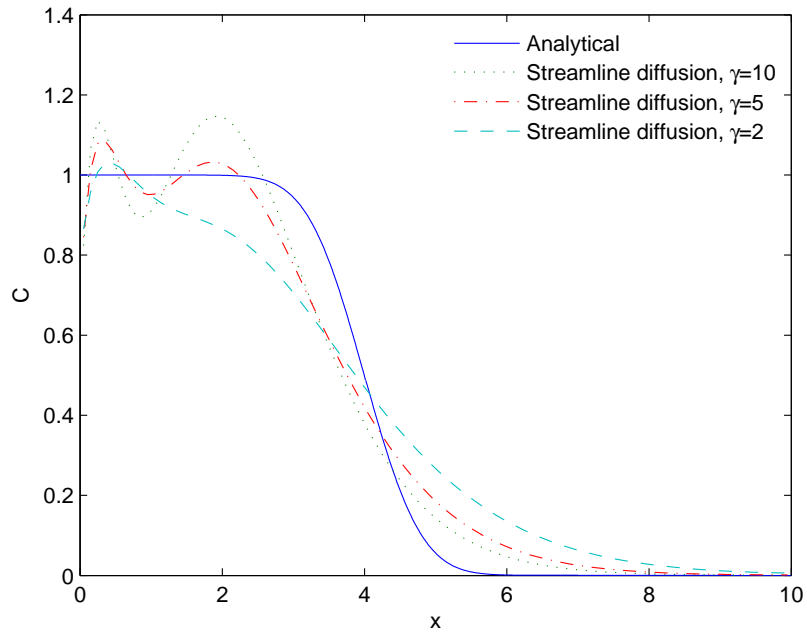
Figure 1.4: Analytical solution compared with numerical solutions obtained using streamline diffusion with varying performance index. For the analytical solution are $v = 1$ cm/hour and $D = 0.05$ cm^2/hour. For the numerical simulations are $\Delta x = 0.1$ cm and $\Delta t = 1$ hour.

into the domain, with the water. If the surface is ponded with water containing a solute, the solute is also moved solely by advection. A little more accurate description could have been obtained if the boundary condition was implemented as a Dirichlet condition which also allowed the solute to be moved by dispersion and diffusion into the soil. It is assessed that the error is insignificant.

When the water moving out of the domain. No solute is following the water. This is for most solutes an good boundary condition - at least for evaporation processes. For a situation with liquid water is leaving the soil through the upper boundary the description is not appropriate, but at present Daisy is not intended for that kind of scenarios. Summarized the upper boundary condition can be expressed as:

$$\left(-\theta_m D_{zz} \frac{\partial C_m}{\partial z} + q_z C_m \right) \Bigg|_{z=z_{\text{surf}}} = q_{\text{out}} C_{\text{surf}} \qquad (1.25)$$

where z_{surf} is the z-coordinate of the soil surface, q_z is the flow (positive upwards) and q_{out} is the flux out of the domain (negative for flux into the domain). C_{surf} is the concentration of the surface water.

Numerically all the types of upper boundary conditions is implemented as explicit Neumann conditions, i.e. the solute movement over the boundary is independent of the solute concentrations in the domain.

1.2.3 Lower boundary condition

The lower boundary condition describes the movement of solute through the lower boundary. If the water have a free drainage condition, there is a flux condition for the solute when the solute is moved out of the domain by advection. If there is specified a groundwater table or aquitard boundary condition, i.e. pressure (Dirichlet) conditions for the water flow, also the solute movement have a Dirichlet condition with a specified concentration at the boundary. For a specified steady-state water flux (mostly used for testing purposes). It is possible both to chose specified concentration (Dirichlet) and flux boundary conditions.

Numerically the Neumann boundary conditions is implemented, either implicit or explicit - implicit when the water flux is outwarded from the lower boundary and the concentration associated with the flux is given by the concentration inside the domain. Explicit when the water moves into the domain and the associated concentration is the concentration outside the domain.

The Dirichlet boundary condition is implemented as a explicit Neumann boundary condition. Based on the solution in the previous timestep the flux is calculated with the given concentration on the boundary. The method is different from the method used for the water movement, but prevents an extra iteration loop inside each timestep with following increased computational times. In the

water movement simulations, the iteration loop was under all circumstances necessary since the equation is non-linear. Otherwise for the solute movement. But with very large concentration gradients (and following large movement by diffusion and dispersion processes) and small cells at the boundary some numerically problems can occur. To prevent this kind of instability, the size of the timesteps can be lowered if also timestep reduction is chosen as stabilizing method to prevent to high $P_e C_r$-numbers. If timestep reduction is chosen, the timestep is reduced so:

- For diffusion into the cell, only half of the volume of the conc difference between border and cell can be transported by diffusion over the boundary into the cell in a timestep.

- For diffusion out from the cell, only half of the volume of the conc difference between cell and border can be transported by diffusion over the boundary out from the cell in a timestep.

To prevent to large computational times, the timestep can not be lower than a chosen a minimum value. If the instabilities are high and produce negative concentrations at the cells at the boundary, the computations in the timestep is repeated and the solute is only moved by advection over the boundary. This can happen if the minimum value of the size of the timesteps is chosen to high.

1.2.4 Verification: One-dimensional flow with retardation and degradation

There are developed a lot of analytical solutions for the one-dimensional convective-dispersive equation, see for example **?**). The equations are developed for situations where the diffusion is constant and the water flow is steady state (i.e. $\partial \theta_m / \partial t = 0$ and constant $\mathbf{q}$). These conditions are seldom fulfilled in the 'real life' where both the water content and the flux are time-dependent. For testing the solute transport model is a situations with steady state water movement simulated.

If the adsorption process is very fast, the amount of adsorbed solute can be expressed with a adsorption isotherm which is a relationship between adsorbed (C_a) and dissolved concentration, C_m. The bulk density is assumed to be constant through time. The two first terms of the left hand side of equation (1.13) can be rewritten as:

$$\rho_b \frac{\partial C_a}{\partial t} + \frac{\partial (C_m \theta)}{\partial t} = \rho_b \frac{\partial C_a}{\partial C} \cdot \frac{\partial C_m}{\partial t} + \theta_m \frac{\partial C_m}{\partial t} + C_m \frac{\partial \theta_m}{\partial t} = \theta R \frac{\partial C_m}{\partial t} + C_m \frac{\partial \theta_m}{\partial t} \tag{1.26}$$

where R often in the literature is called the *Retardation factor*:

$$R = \frac{\rho_b}{\theta_m} \cdot \frac{\partial C_a}{\partial C_m} + 1 \tag{1.27}$$

The most simple adsorption isotherm is the linear adsorption where $C_a = K_d C_m$ and as a consequence $R = 1 + \frac{\rho_b K_d}{\theta_m}$.

Zero or first order kinetics are included in the model. In zero order kinetics, the velocity of the reaction is independent of the concentration and in 1.st order kinetics the reaction velocity is proportional to the concentration. Thus the advection dispersion equation yields:

$$R\theta_m \frac{\partial C_m}{\partial t} + C_m \frac{\partial \theta_m}{\partial t} = -\nabla \cdot (C_m \mathbf{q}_m - \theta_m \mathbf{D}\nabla C_m) - \theta_m \mu_l C_m + \rho_b \mu_s \quad (1.28)$$

where the second last term represents a first order production in the liquid phase. μ_l is the rate constant. An often-used term is the half-life. In a batch experiment the half-life is the time required for the mass of reacting materiel to decrease to half the original mass. The reaction half-life can be calculated as $t_{1/2} = ln(2)/\mu_l$. The equation can be used for many chemical processes, and for radioactive decay. The last term on the right hand side of equation (1.29) represents a zero order removal from the solid to the liquid phase. μ_s is the rate constant for the zero order process. In **?**) is considered a one-dimensional case with degradation of both zero and first order. The governing differential equation can then be expressed as:

$$R\frac{\partial C_m}{\partial t} = D\frac{\partial^2 C_m}{\partial x^2} - v\frac{\partial C_m}{\partial x} - \mu C_m + \gamma \quad (1.29)$$

where μ is the rate constant for first order decay in the liquid and γ represents the similar rate constant for zero-order production:

For the simulation, the initial condition is

$$C_m(x, 0) = C_{m,i} \quad (1.30)$$

and the upper boundary condition is

$$\left(-D\frac{\partial C_m}{\partial x} + vC_m\right)\bigg|_{x=0} = vC_{m,0} \quad (1.31)$$

The solution is

$$C_m = \frac{\gamma}{\mu} + (C_{m,i} - \frac{\gamma}{\mu})A(x, t) + (C_{m,0} - \frac{\gamma}{\mu})B(x, t), 0 < t \le t_0 \quad (1.32)$$

where $A(x, t)$ and $B(x, t)$ can be calculated as

$A(x, t) = \exp(-\mu t/R)\cdot$

$$\left\{1 - \frac{1}{2}\operatorname{erfc}\left[\frac{Rx - vt}{2(DRt)^{1/2}}\right] - \left(\frac{v^2 t}{\pi DR}\right)^{1/2}\exp\left[-\frac{(Rx - vt)^2}{4DRt}\right]\right. \quad (1.33)$$

$$\left. + \frac{1}{2}\left(1 + \frac{vx}{D} + \frac{v^2 t}{DR}\right)\exp(vx/D)\operatorname{erfc}\left[\frac{Rx + vt}{2(DRt)^{1/2}}\right]\right\}$$

$$B(x,t) = \frac{v}{v+u} \exp\left[\frac{(v-u)x}{2D}\right] \mathrm{erfc}\left[\frac{Rx-ut}{2(DRt)^{1/2}}\right] +$$

$$\frac{v}{v-u} \exp\left[\frac{(v+u)x}{2D}\right] \mathrm{erfc}\left[\frac{Rx+ut}{2(DRt)^{1/2}}\right] + \qquad (1.34)$$

$$\frac{v^2}{2\mu D} \exp\left[\frac{vx}{D} - \frac{\mu t}{R}\right] \mathrm{erfc}\left[\frac{Rx+vt}{2(DRt)^{1/2}}\right]$$

with

$$u = v\sqrt{1 + \frac{4\mu D}{v^2}} \qquad (1.35)$$

For comparing the analytical solution with the Daisy solution is chosen an situation with $v = 10$ cm/day, $D = 5$, $\gamma = 0.2$ and $\mu = 0.5$. For the Daisy simulation is there used a vertical column which is 100 cm high and 1 cm wide. The grid consisting of 100 1 X 1 cm cells. For the Daisy-modeling is used a similar mesh as in the previous example just 100 cm long (and double so many elements). The length of the timesteps, $\Delta t = 1/10$ day. In figure 1.5 is the Daisy solution compared with the above described analytical solution. As it can be seen are the solutions quite coincident.

Figure 1.5: Comparison between analytical and Daisy simulation of a process with both zero and first order degradation.