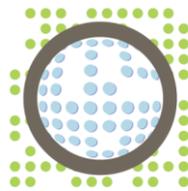


Applied 3-D Groundwater Modeling with MODFLOW / MT3D / MT3DMS

-

Transport Modeling



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Transport models

- based on flow models
- interpolation of concentrations measurements (point information)
- balancing of solute fluxes
- evaluation of tracer tests
- prediction of contaminant spreading
- monitoring of in situ remediation measures
- insight in evolution of groundwater quality

⇒ Just as flow models transport models are mechanistically based. However, the mechanisms are more complicated than that of the flow models. Flow modeling is state-of-the-art today, while transport modeling is still exceptional.

Transport mechanisms

Advection

Advection means the movement of solutes caused by groundwater flow. The term convection is usually used if groundwater flow is caused by density or temperature gradients. However, both terms are not always clearly separated from each other. Advection is the transport along pathlines. Therefore pure advective transport can be calculated immediately from results of the flow model with so called pathline models. This requires no further solution of equations or equation systems as the pore velocity u , which determines the advective flux, can be derived directly from interpolation of the known specific cell fluxes Q :

$$Q = -A k_f I$$

with A = Cross-sectional area for water flux [L^2]

$$k_f = \text{hydraulic conductivity [L T}^{-1}\text{]}$$

$$q = \frac{Q}{A}$$

with q = specific flux or Darcy-velocity or filter velocity [$L T^{-1}$]

$$u = \frac{q}{n_e}$$

with u = pore velocity [$L T^{-1}$]

$$n_e = \text{effective porosity [-]}$$

Analytical solutions for pathlines can be provided for simple boundary conditions and model geometry.

Diffusion

Molecular diffusion (Brownian motion) is a mixing process on the molecular level. It results from random movement of molecules and leads to an offset of concentration differences. Dif-

diffusive mass flux is proportional to the driving concentration gradient. The proportionality constant is the coefficient of molecular diffusion. Diffusive flux is described by FICKS law:

$$J = -D_m \frac{\partial c}{\partial n}$$

with J = diffusive flux [$M L^{-2} T^{-1}$]

D_m = coefficient of molecular diffusion [$L^2 T^{-1}$]

$\Delta c / \Delta n$ = concentration gradient [$M L^{-3} L^{-1}$]

Molecular diffusion is a relatively slow process. The coefficient of molecular diffusion for dissolved ions is roughly $10^{-9} m^2 s^{-1}$. The magnitude of diffusive transport can be estimated with the help of a strongly simplified calculation (e.g. Neretnikes, 2002):

$$l = 2.2 \sqrt{D_m t}$$

with l = distance of diffusive transport for which the mean concentration equals 50% of the maximum concentration [L]

t = typical time [T]

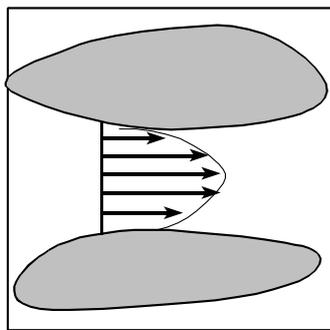
Setting $t = 1$ year leads to $l = 40$ cm, i.e. the typical diffusive transport velocity is in the order of some decimeters per year. For comparison the typical advective transport velocity in porous aquifers is usually in the order of 100 m per year.

Dispersion

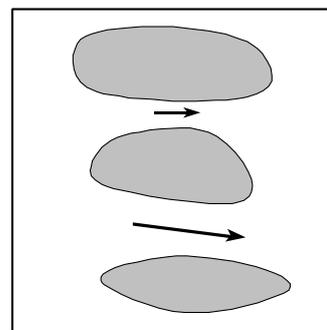
Advection and diffusion are the only effective processes on the pore scale. However, as for groundwater flow the description of transport processes on the pore scale is not feasible in a groundwater model. Instead a continuum approach on the basis of a representative elementary volume (REV) is used.

Inside a single pore velocity differences arise because of an approximately parabolic velocity profile between the pore walls. Furthermore mean pore velocities may differ from pore to pore because of different pore diameters. This velocity distribution leads to a smearing of sharp fronts. As the velocity distribution is not resolved in the REV but represented by a sin-

gle mean velocity, the observed front spreading has to be accounted for in form of an additional mixing term, called **microscopic or pore scale dispersion**. The following figure illustrates the principal mechanisms:

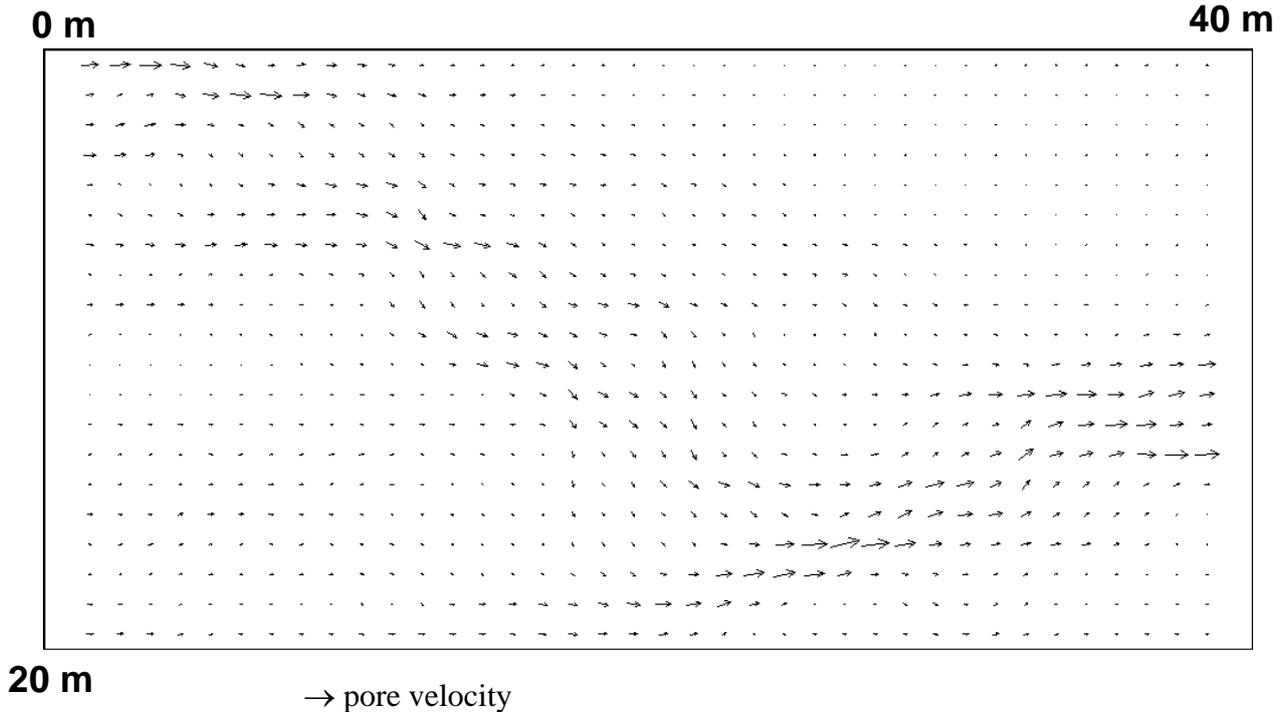


Velocity distribution in a single pore



velocity distribution between pores

Pore scale dispersion and molecular diffusion would be the only effective mixing processes in a completely homogeneous aquifer. Real aquifers, however, are always heterogeneous. The heterogeneity leads to a non uniform velocity distribution and thus to smearing of fronts above the pore scale. This additional mixing process is called **macro-dispersion**.



Theoretically the velocity distribution above the pore scale could be explicitly resolved in a groundwater model instead of using the macro-dispersion concept. However, this would require knowledge on the detailed structure of the aquifer, which usually is not available. When asymptotic conditions are reached after a certain travel distance, the mixing processes caused by dispersion can be described analogous to Fickian diffusion:

$$J = -D \frac{\partial c}{\partial n}$$

with J = dispersive flux [$M L^{-2} T^{-1}$]

D = dispersion coefficient [$L^2 T^{-1}$]

M_c/M_n = concentration gradient [$M L^{-3} L^{-1}$]

Like molecular diffusion dispersion is an irreversible process. However, there are a number of important differences between diffusion and dispersion:

- In general the dispersion coefficient is orders of magnitude larger than the coefficient of

molecular diffusion

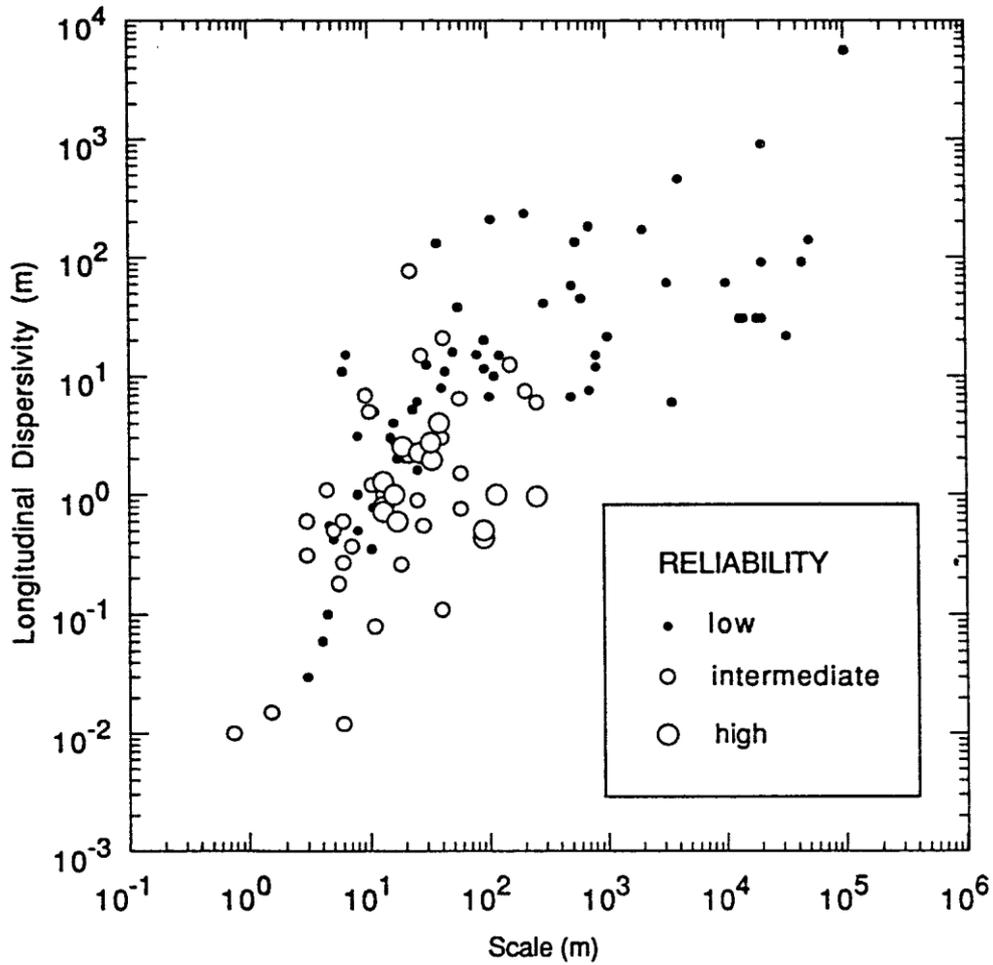
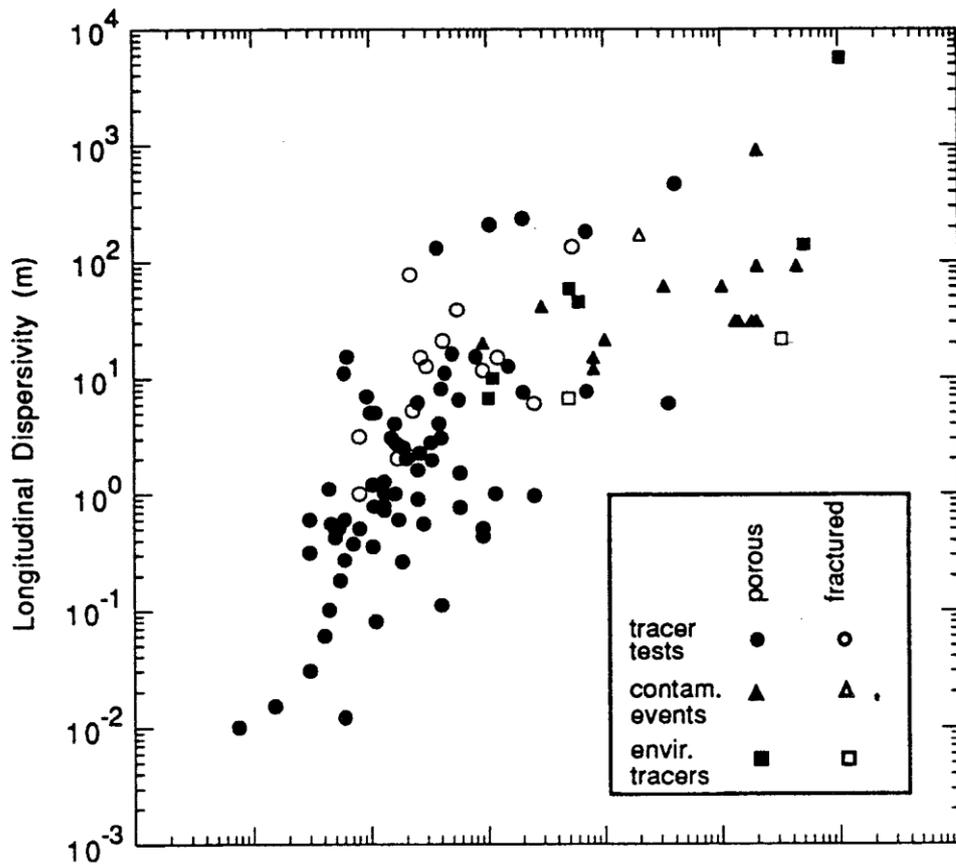
- Molecular diffusion is an isotropic process, whereas dispersion shows anisotropic behavior already in an otherwise isotropic ideal medium with dispersion in flow direction being always larger than transverse dispersion
- The coefficient of molecular diffusion is independent of the scale of observation, whereas the dispersion coefficient is a scaling value, i.e. it increases with increasing scale of observation
- The dispersion coefficient depends on the pore velocity. It can be calculated using the so-called dispersivity α (a mixing path):

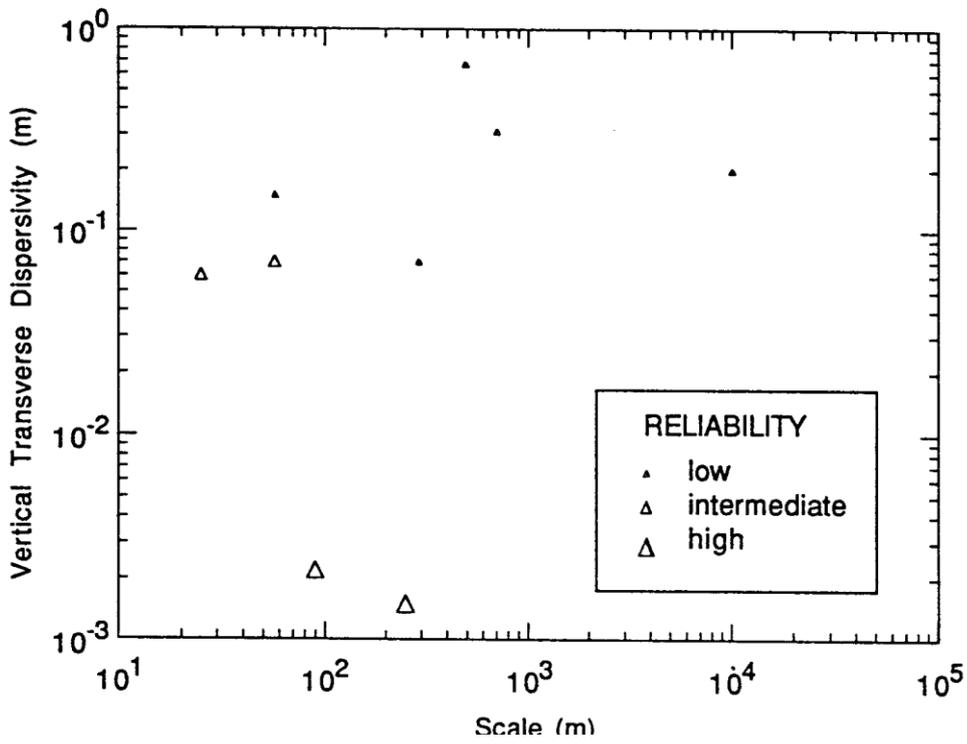
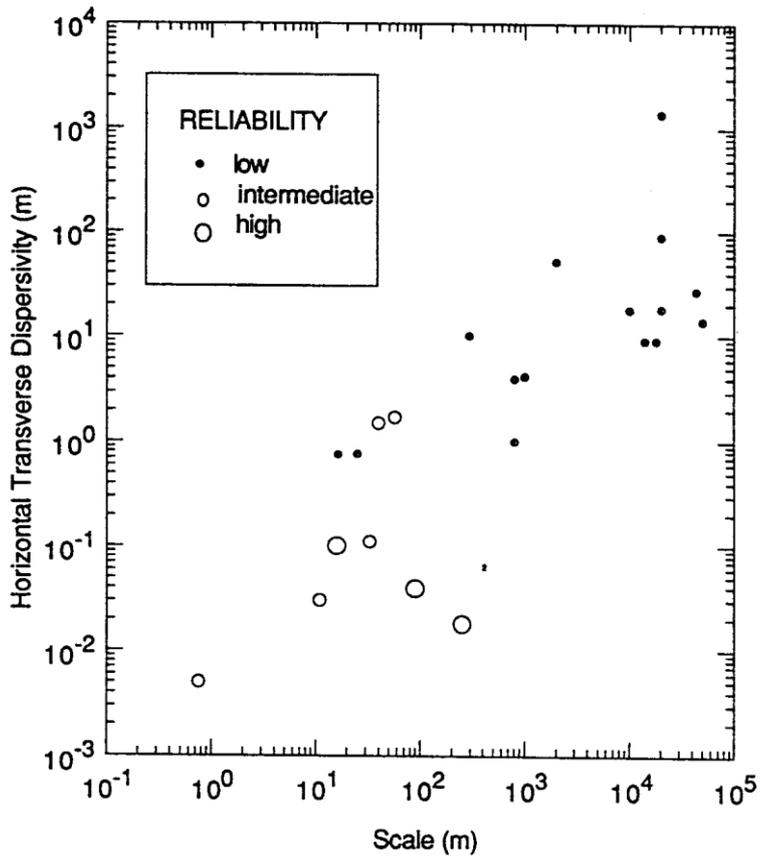
$$D = \alpha u$$

with α = dispersivity [L]

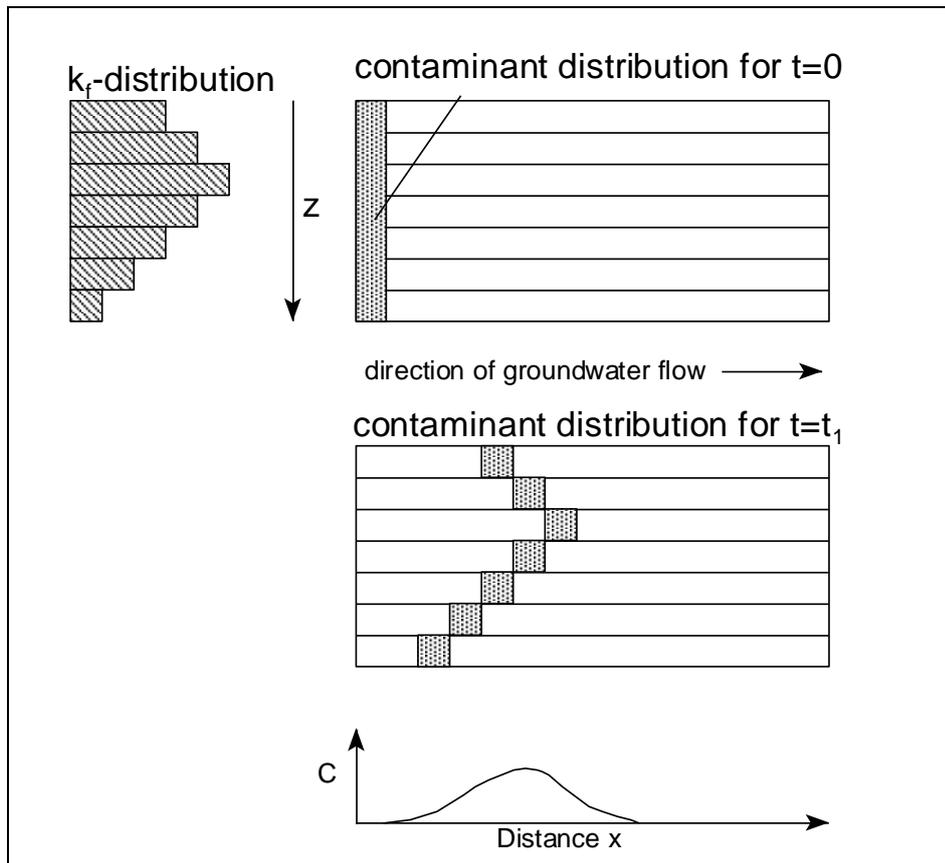
u = pore velocity [L T⁻¹]

The dispersivity is a porous medium property. Its value depends on the degree of aquifer heterogeneity and on the integral transport scale. In homogeneous single grained sands the dispersivity is in the order of the pore diameter, while it may become very large in natural aquifers. The empirical relation between the scale of observation and the dispersivity is illustrated by the following figures taken from Gelhar et al. (1992):





Dispersion can be considered as differential advection. It should be noted here that it is molecular diffusion which finally makes up the mixing process, but dispersion increases the surface area and thus the overall diffusive fluxes (fig. after Kinzelbach, 1992):



Dispersion is usually quantitatively much more important for solute transport in the aquifer model than diffusion, as can be gathered from the following considerations:

A dispersivity of roughly 10 m can be assumed for solute transport over a few hundred meters. With a mean pore velocity of $1 \text{ m d}^{-1} = 1.16 \times 10^{-5} \text{ m s}^{-1}$ this yields a dispersion coefficient of $1.16 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ which is 5 orders of magnitude larger than the coefficient of molecular diffusion.

Reaction

Besides advection and diffusion/dispersion most compounds dissolved in water are subject to chemical or biochemical reactions including adsorption/desorption, degradation/decay, and

dissolution/precipitation. Some specific reactions will be presented later. For the next chapters we will restrict the descriptions on transport of non-reactive, hydrodynamically passive solutes. Non-reactive means that the solutes do not undergo any reactions, while hydrodynamically passive means that solute concentrations are such small that water density or viscosity are not affected, i.e. that there is no back-coupling between transport and flow.

Transport equation

The transport equation for a non-reactive solute can be derived from mass balance considerations in a control volume (e.g. the REV). Then the following mass fluxes are obtained:

§ advective mass flux:

$$j_a = u c V_w$$

with j_a = advective mass flux (j_{ax}, j_{ay}, j_{az}) [$M L T^{-1}$]

u = pore velocity (u_x, u_y, u_z) [$L T^{-1}$]

c = solute concentration [$M L^{-3}$]

V_w = effective water volume contributing to solute transport [L^3]

§ dispersive/diffusive mass flux:

$$j_d = -(D_m \mathbf{1} + D) \nabla c V_w$$

with j_d = dispersive/diffusive mass flux (j_{dx}, j_{dy}, j_{dz}) [$M L T^{-1}$]

D_m = coefficient of molecular diffusion [$L^2 T^{-1}$]

$$\mathbf{1} = \text{Identity matrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} [-]$$

D = dispersion tensor [$L^2 T^{-1}$]

Λ = nabla operator in three dimensions ($M/M_x, M/M_y, M/M_z$)

§ For reasons of mass conservation any change in the advective or dispersive/diffusive mass flux j_a and j_d over the surface of the control volume must be balanced by storage change inside the control volume or by external sources and sinks:

$$S = \frac{\partial(c V_w)}{\partial t} = -\nabla j_a - \nabla j_d + \sigma V_G$$

with S = storage inside the control volume per unit time [$M T^{-1}$]

σ = external source/sink [$M L^{-3} T^{-1}$]

§ Inserting the advective and dispersive mass fluxes leads to:

$$\frac{\partial(c V_w)}{\partial t} = -\nabla(u c V_w) + \nabla((D_m 1 + D) \nabla c V_w) + \sigma V_G$$

§ Division by V_G and with $V_w / V_G = n_e$ (effective porosity) provides the general transport equation in 3 dimensions for non-reactive species:

$$\frac{\partial(c n_e)}{\partial t} = -\nabla(u c n_e) + \nabla((D_m 1 + D) \nabla c n_e) + \sigma$$

§ Setting $n_e = \text{constant}$ and ignoring molecular diffusion leads to:

$$\frac{\partial c}{\partial t} = -\nabla(u c) + \nabla(D \nabla c) + \frac{\sigma}{n_e}$$

§ Deviation of the advection term gives:

$$\nabla(u c) = \nabla u c + \nabla c u$$

The term $\nabla u c$ describes a change in the advective mass flux caused by a change in the pore velocity. For a spatially constant effective porosity n_e this means that water must have been injected into or extracted from the control volume. Therefore $\nabla u c$ can be treated as an external source/sink term:

$$\frac{\partial c}{\partial t} = -u \nabla c + \nabla(D \nabla c) + \frac{\sigma}{n_e} + \frac{w}{n_e} c_Z$$

with σ = external source/sink term not coupled to water flux [$M L^{-3} T^{-1}$]

w = injection/extraction of water applied to the control volume [$M L^{-3} T^{-1}$]

c_Z = concentration of the incoming water ($c_Z = c$ in case of water extraction) [$M L^{-3}$]

The dispersion tensor

As dispersion is always an anisotropic process, the dispersion coefficient in 2 or 3 dimensions

must always be expressed in form of a tensor. Simple expressions for this tensor can only be derived for certain simplified aquifer situations. In an isotropic three-dimensional aquifer one longitudinal (α_l) and one transverse dispersivity (α_t) can be distinguished:

$$\mathbf{D} = \begin{pmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{pmatrix}$$

The off-diagonal components of the tensor, e. g. D_{xy} and D_{xz} , allow for a dispersive mass flux in x-direction caused by concentration gradients in y- und z-direction:

$$j_{d,x} = -D_{xx} \frac{\partial c}{\partial x} - D_{xy} \frac{\partial c}{\partial y} - D_{xz} \frac{\partial c}{\partial z}$$

If the x-axis is orientated parallel to the flow direction all components except that on the diagonal become zero:

$$\mathbf{D} = \begin{pmatrix} D_{xx} & 0 & 0 \\ 0 & D_{yy} & 0 \\ 0 & 0 & D_{zz} \end{pmatrix}$$

Numerical solution of the transport equation

Analytical solutions of the transport equation exist for special cases with simple boundary conditions only. In case of arbitrary boundary conditions and aquifer parameter distributions the transport equation has to be solved numerically.

While only temporal derivations ($\partial h/\partial t$) and second order derivations in space ($\partial^2 h/\partial x^2$) occur in the flow equation, the transport equation includes temporal derivations ($\partial c/\partial t$), a second order derivation in space ($\partial^2 c/\partial x^2$) from dispersion, and an additional first order spatial derivation term ($\partial c/\partial x$) from advection. This combination of first and second order terms complicates the numerical solution of the transport equation.

Differential equations consisting of second order spatial terms only are called parabolic differential equations. Examples are the flow equation and the diffusion equation. So-called Eulerian methods with a fixed grid like the finite difference (FD) or the finite element (FE) method are well suited for the numerical processing of these equations.

A differential equation consisting of first order spatial terms only are called hyperbolic differential equations. The pure advective transport equation (without dispersion) represents an equation of this kind. Suitable numerical methods in this case are the so-called Lagrangian methods which have no fixed grids. Instead they track the transport of particles along pathlines. Therefore these methods are also called particle tracking methods.

The complete transport equation is of mixed type. It receives a hyperbolic contribution from advection and a parabolic contribution from dispersion. According to this hybrid nature neither Eulerian nor Lagrangian methods are optimally suited for the processing of the transport equation. MT3D or MT3DMS provide both pure Eulerian (FD and TVD) and mixed Eulerian-Lagrangian methods (MOC, MMOC, HMOC). The latter use a particle tracking method to simulate advective transport and the standard finite difference method to simulate dispersive transport. The three particle tracking methods vary only in the treatment of the advective transport, while dispersive transport is always treated in the same way. Pure Lagrangian methods like the Random-Walk method are not implemented in MT3D or MT3DMS.

In the following the different available methods and their assets and drawbacks are presented. A special emphasis is put on the FD method, as it allows to easily exemplify basic concepts, while the other methods are presented somewhat more briefly. Temporal discretisation and numerical stability and accuracy criteria are discussed along with the FD method. However, these issues are also relevant for many of the other methods. A more detailed description of the different methods can be found in Zheng and Wang (1999).

The finite difference method (FD)

The differential equations for solute transport are replaced by differences in space and time:

$$\frac{\partial c}{\partial x} \approx \frac{\Delta c}{\Delta x} = \frac{c_2 - c_1}{x_2 - x_1}$$

$$\frac{\partial c}{\partial t} \approx \frac{\Delta c}{\Delta t} = \frac{c_2 - c_1}{t_2 - t_1}$$

The application of differences instead of differentials requires that the model area has to be discretised on a model grid. This implies that concentrations are no longer calculated continuously in the model area, but for discrete grid points (nodes) only. The temporal continuum is in the same way replaced by discrete points in times for which new concentrations are calculated.

The problem consists in solving the general transport equation:

$$\frac{\partial(n_e c)}{\partial t} = -\nabla(u n_e c) + \nabla((D_m + D) n_e \nabla c) + \sigma$$

The FD method can be derived intuitively by establishing the nodal mass balance:

nodal storage per time step

=

change of advective flux

+

change of dispersive flux

+

mass change via external sinks/sources not coupled to water flow

Discretisation of the two-dimensional transport equation

The detailed description of the FD method in three dimensions would be too extensive. Therefore the discretisation is explained for the two dimensional case, but it can be easily transferred in 3D.

We have to solve the following differential equation:

$$\frac{\partial(n_e c)}{\partial t} = -\frac{\partial(u_x n_e c)}{\partial x} - \frac{\partial(u_y n_e c)}{\partial y}$$

$$+ \frac{\partial\left(D_{xx} n_e \frac{\partial c}{\partial x} + D_{xy} n_e \frac{\partial c}{\partial y}\right)}{\partial x} + \frac{\partial\left(D_{yy} n_e \frac{\partial c}{\partial y} + D_{yx} n_e \frac{\partial c}{\partial x}\right)}{\partial y}$$

$$+ \sigma$$

Scheidegger (1961) provided an expression for the dispersion tensor:

$$D_{xx} = \alpha_l \frac{u_x^2}{u} + \alpha_t \frac{u_y^2}{u}$$

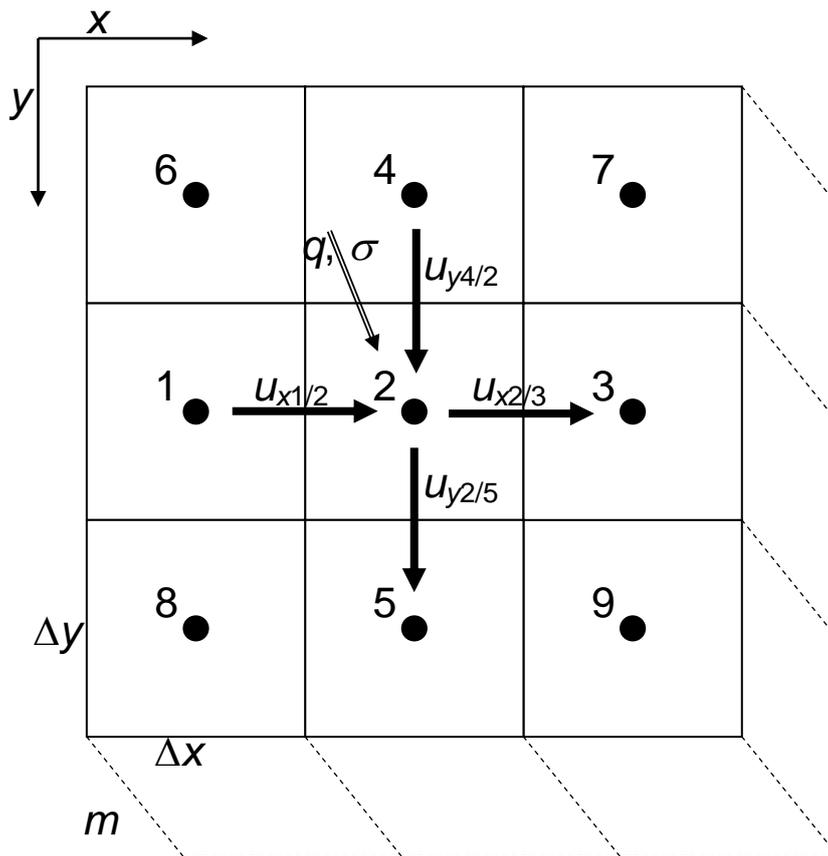
$$D_{yy} = \alpha_t \frac{u_x^2}{u} + \alpha_l \frac{u_y^2}{u}$$

$$D_{xy} = D_{yx} = (\alpha_l - \alpha_t) \frac{u_x u_y}{u}$$

with

$$u = |u| = \sqrt{u_x^2 + u_y^2}$$

Mass balance for the two-dimensional case



- Solute mass storage for node 2:

$$\Delta S_2 = \frac{c_2(t + \Delta t) - c_2(t)}{\Delta t} \Delta x_2 \Delta y_2 m_2 n_{e,2}$$

- Advective fluxes for node 2:

$$a_{x1/2} = u_{x1/2} n_{e1/2} c_{1/2} \Delta y_{1/2} m_{1/2}$$

$$a_{x2/3} = u_{x2/3} n_{e2/3} c_{2/3} \Delta y_{2/3} m_{2/3}$$

$$a_{y4/2} = u_{y4/2} n_{e4/2} c_{4/2} \Delta x_{4/2} m_{4/2}$$

$$a_{y2/5} = u_{y2/5} n_{e2/5} c_{2/5} \Delta x_{2/5} m_{2/5}$$

Change of the advective flux:

$$\Delta a_{x2} = a_{x2/3} \quad a_{x1/2} = u_{x2/3} n_{e2/3} c_{2/3} \Delta y_{2/3} m_{2/3} - u_{x1/2} n_{e1/2} c_{1/2} \Delta y_{1/2} m_{1/2}$$

$$\Delta a_{y2} = a_{y2/5} \quad a_{y4/2} = u_{y2/5} n_{e2/5} c_{2/5} \Delta x_{2/5} m_{2/5} - u_{y4/2} n_{e4/2} c_{4/2} \Delta x_{4/2} m_{4/2}$$

Using an "**upwind**"-weighted scheme (backward differences) means that c_1 is used for $c_{1/2}$ and c_4 for $c_{4/2}$ (if u is positive in x - and y -direction).

Central -weighting means that the arithmetic mean from c_1 and c_2 ($[c_1+c_2]/2$) is used for $c_{1/2}$ and the arithmetic mean from c_2 and c_4 ($[c_2+c_4]/2$) for $c_{2/4}$.

MT3D always uses an upwind scheme, while MT3MS provides both upwind and central difference schemes.

- Solute mass change in connection with a water extraction or injection for node 2:

$$\Delta q_2 = w_2 \Delta x_2 \Delta y_2 m_2 c_z$$

- Dispersive fluxes for node 2:

Diagonal terms:

$$d_{xx1/2} = D_{xx1/2} \frac{c_2 - c_1}{\Delta x_{1/2}} \Delta y_{1/2} n_{e1/2} m_{1/2}$$

$$d_{xx2/3} = D_{xx2/3} \frac{c_3 - c_2}{\Delta x_{2/3}} \Delta y_{2/3} n_{e2/3} m_{2/3}$$

$$d_{yy4/2} = D_{yy4/2} \frac{c_2 - c_4}{\Delta y_{4/2}} \Delta x_{4/2} n_{e4/2} m_{4/2}$$

$$d_{yy2/5} = D_{yy2/5} \frac{c_5 - c_2}{\Delta y_{2/5}} \Delta x_{2/5} n_{e2/5} m_{2/5}$$

Cross terms:

Dispersive flux in x-direction caused by a concentration gradient in y-direction:

One possibility to determine the effective concentration gradient in y-direction is:

$$\begin{aligned}\Delta c_{xy1/2} &= \frac{I}{2} \left(\frac{c_8 - c_6}{\Delta y_{6/1} + \Delta y_{1/8}} + \frac{c_5 - c_4}{\Delta y_{4/2} + \Delta y_{2/5}} \right) \\ &= \frac{I}{2} \left(\frac{c_8 - c_6 + c_5 - c_4}{\Delta y_{6/1} + \Delta y_{1/8}} \right)\end{aligned}$$

$$\Delta c_{xy2/3} = \frac{I}{2} \left(\frac{c_5 - c_4 + c_9 - c_7}{\Delta y_{6/1} + \Delta y_{1/8}} \right)$$

The resulting fluxes are:

$$d_{xy1/2} = D_{xy1/2} \Delta c_{xy1/2} \Delta y_{1/2} n_{e1/2} m_{1/2}$$

$$d_{xy2/3} = D_{xy2/3} \Delta c_{xy2/3} \Delta y_{2/3} n_{e2/3} m_{2/3}$$

Dispersive flux in y-direction because of a concentration gradient in x-direction:

One possibility to determine the effective concentration gradient in x-direction is:

$$\begin{aligned}\Delta c_{yx4/2} &= \frac{I}{2} \left(\frac{c_7 - c_6}{\Delta x_{6/4} + \Delta x_{4/7}} + \frac{c_3 - c_1}{\Delta x_{1/2} + \Delta x_{2/3}} \right) \\ &= \frac{I}{2} \left(\frac{c_7 - c_6 + c_3 - c_1}{\Delta y_{6/4} + \Delta y_{4/7}} \right)\end{aligned}$$

$$\Delta c_{yx2/5} = \frac{I}{2} \left(\frac{c_3 - c_1 + c_9 - c_8}{\Delta y_{6/4} + \Delta y_{4/7}} \right)$$

The resulting fluxes are:

$$d_{yx4/2} = D_{yx4/2} \Delta c_{yx4/2} \Delta x_{4/2} n_{e4/2} m_{4/2}$$

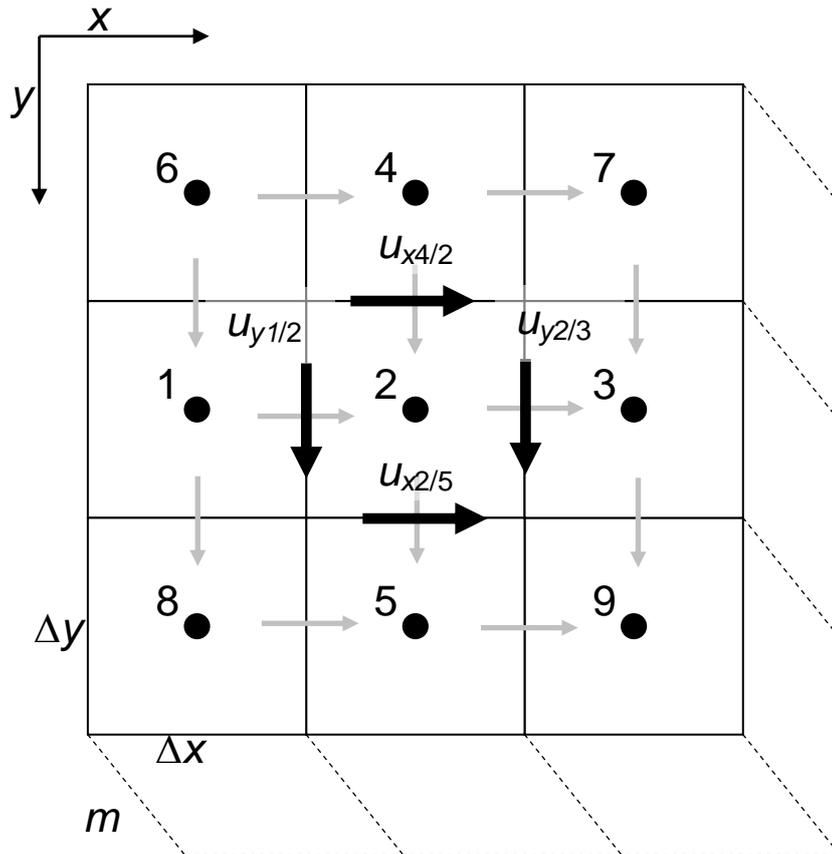
$$d_{yx2/5} = D_{yx2/5} \Delta c_{yx2/5} \Delta x_{2/5} n_{e2/5} m_{2/5}$$

Total change of dispersive flux:

$$\Delta d_{x,2} = d_{xx2/3} - d_{xx1/2} + d_{xy2/3} - d_{xy1/2}$$

$$\Delta d_{y,2} = d_{yy2/5} - d_{yy4/2} + d_{yx2/5} - d_{yx4/2}$$

Besides the velocities that can be immediately derived from the flow model results further velocities on intermediate locations are needed for the calculation of the dispersion coefficients. The additional velocities have to be estimated by interpolation:



$$D_{xx,1/2} = \frac{\alpha_l u_{x,1/2} + \alpha_t u_{y,1/2}}{u}$$

$$u_{y,1/2} = \frac{u_{y,6/1} + u_{y,4/2} + u_{y,1/8} + u_{y,2/5}}{4}$$

$$u = \sqrt{u_{x,1/2}^2 + u_{y,1/2}^2}$$

$$D_{xx,2/3} = \frac{\alpha_l u_{x,2/3} + \alpha_t u_{y,2/3}}{u}$$

$$u_{y,2/3} = \frac{u_{y,4/2} + u_{y,7/3} + u_{y,2/5} + u_{y,3/9}}{4}$$

$$u = \sqrt{u_{x,2/3}^2 + u_{y,2/3}^2}$$

$$D_{yy,4/2} = \frac{\alpha_t u_{x,4/2} + \alpha_l u_{y,4/2}}{u}$$

$$u_{x,4/2} = \frac{u_{x,6/4} + u_{x,4/7} + u_{x,1/2} + u_{x,2/3}}{4}$$

$$u = \sqrt{u_{x,4/2}^2 + u_{y,4/2}^2}$$

$$D_{yy,2/5} = \frac{\alpha_t u_{x,2/5} + \alpha_l u_{y,2/5}}{u}$$

$$u_{x,2/5} = \frac{u_{x,8/5} + u_{x,5/9} + u_{x,1/2} + u_{x,2/3}}{4}$$

$$u = \sqrt{u_{x,2/5}^2 + u_{y,2/5}^2}$$

$$D_{xy,1/2} = \frac{(\alpha_l - \alpha_t) u_{x,1/2} u_{y,1/2}}{u}$$

$$D_{xy,2/3} = \frac{(\alpha_l - \alpha_t) u_{x,2/3} u_{y,2/3}}{u}$$

$$D_{yx,4/2} = \frac{(\alpha_l - \alpha_t) u_{x,4/2} u_{y,4/2}}{u}$$

$$D_{yx,2/5} = \frac{(\alpha_l - \alpha_t) u_{x,2/5} u_{y,2/5}}{u}$$

- Solute mass change not connected to water flux at node 2:

$$\Delta M_2 = \sigma_2 \Delta x_2 \Delta y_2 m_2$$

The above mentioned single items of the mass balance can be assembled to the overall mass balance for node 2:

$$\Delta S_2 = -\Delta a_{x,2} - \Delta a_{y,2} + \Delta q_2 + \Delta d_{x,2} + \Delta d_{y,2} + \Delta M_2$$

The discrete transport equation must be solved for each node and every time step. To accomplish this the local indices have to be replaced by global indices, i.e. c_2 becomes $c_{i,j}$, c_1 becomes $c_{i-1,j}$, c_3 becomes $c_{i+1,j}$, c_4 becomes $c_{i,j-1}$ and c_5 becomes $c_{i,j+1}$ etc.

Temporal discretisation

There are different possibilities to perform the temporal discretisation, e.g.:

- **Explicit** method: The concentrations c at the beginning of the time step t are used for the spatial differences. Then the new concentrations at the end of the time step $t + \Delta t$ appear only once in the storage term. Therefore the nodal equations can be solved independently. The explicit method has the advantage that it is easy to program and that the computer storage demand is low. However, one has to observe very strict stability criteria and therefore has to use very small time steps in general. This may lead to a huge number of simulation steps and thus to a large computational effort. MT3D employs exclusively an explicit scheme.
- **Implicit** method: All concentrations c of the spatial difference terms are taken at the end of the time step $t + \Delta t$. Therefore the new concentrations at node i depend on the new concentrations at node $i-1$ and node $i+1$ and the nodal equations can no longer be solved separately. Instead an equation system with n equations for n unknowns has to be solved for each node. Because of the usually large size of the equation system for 3-dimensional problems and implicit formulations direct equation solvers are usually not applicable and iterative equation solvers are used. MT3DMS provides both explicit and implicit discretisation schemes.

Initial and boundary conditions

Solving the partial differential equations of solute transport is an initial and boundary value

problem. Therefore an initial concentration has to be provided for each node for $t=0$. For the subsequent time steps the results of the previous time steps are taken as initial values. A steady state solution independent of the initial values, which can be found for the flow equation, does often not exist for the numerical solution of the transport problem.

3 types of **boundary conditions** can be considered:

- first type or prescribed concentration boundary, where the concentration at a given node is fixed.
- second type boundary condition (prescribed dispersive flux boundary). This boundary condition is of particular interest at no flow boundaries of the flow model where dispersive fluxes might occur. In MT3D and MT3DMS dispersive fluxes are ignored on no flow boundaries (completely impermeable boundary).
- third type boundary condition (prescribed total solute flux). This boundary condition may be realized in MT3D and MT3DMS by applying injection wells and a given solute concentration of the injection water.

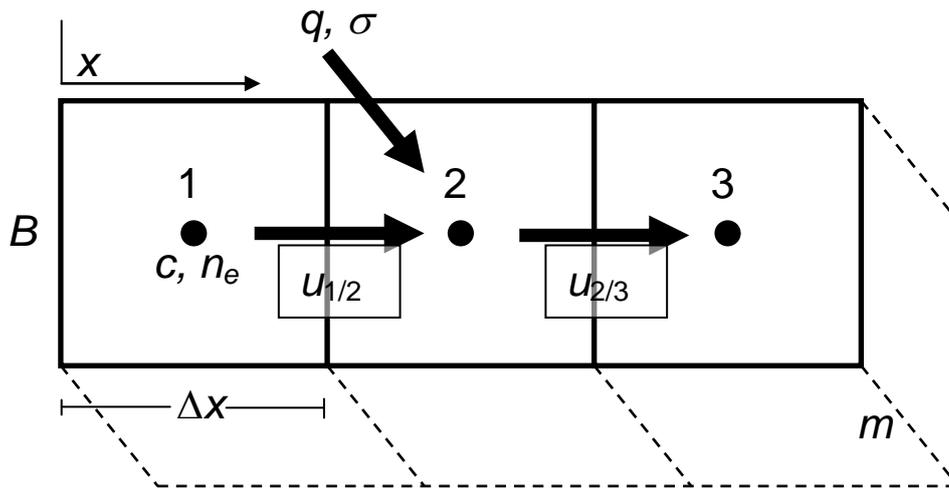
Of special importance is an outflow boundary realized by prescribed heads. The dispersive flux remains unknown here as the solute concentration outside the model area and thus the “last” concentration gradient is not known. In such a case dispersive fluxes are either completely suppressed in the model or a so-called **transmission boundary** is used. Here the last known gradient is linearly extrapolated. This is employed by MT3D and MT3DMS.

Numerical stability conditions

Courant condition:

$$Co, i = \left| \frac{\Delta t u_i}{\Delta i} \right| \quad i = x, y, z$$

The Courant number Co must be less than 1 for explicit solution schemes. Otherwise the solution becomes unstable. The meaning of the Courant condition may be derived intuitively considering a one-dimensional column consisting of 3 cells:



Solute flux from node 1 to node 2 during the time interval Δt using upwind weighting and ignoring dispersion becomes:

$$\dot{M}_{a,12} = n_e u B m c_1 \Delta t$$

The corresponding solute mass increase for node 2 is:

$$\dot{M}_{a,2} = n_e B m \Delta x \Delta c$$

For reasons of mass conservation the two mass changes must be equal:

$$u B m c_1 \Delta t = B m \Delta x \Delta c$$

Transformation leads to:

$$\frac{u \Delta t}{\Delta x} = \frac{\Delta c}{c_1}$$

and:

$$\frac{u \Delta t}{\Delta x} = Co \leq 1$$

Obeying to the Courant condition requires very small time steps in the explicit solution scheme.

Neumann condition:

The Neumann condition vividly means that a concentration gradient must not be reverted by diffusive/dispersive transport. Like the Courant condition the Neumann condition can be de-

rived intuitively. We consider node 2 and assume that the concentration gradient $c_2 - c_1$ is equal to the gradient $c_2 - c_3$. The dispersive transport from the two adjacent nodes into node 2 can be written as:

$$\dot{M}_{d,123} = 2 n_e D \frac{\Delta c_x}{\Delta x} B m \Delta t$$

If we neglect advective transport, the dispersive solute flux must be equaled by a corresponding solute mass increase in node 2:

$$2 n_e D \frac{\Delta c_x}{\Delta x} B m \Delta t = n_e \Delta c_t B m \Delta x$$

Transformation immediately leads to the Neumann condition:

$$\frac{D}{\Delta x^2} \Delta t = \frac{\Delta c_t}{2 \Delta c_x} \leq \frac{1}{2}$$

Courant-Neumann condition:

Bear (1979) combined the Courant and the Neumann condition to simultaneously consider advective and dispersive transport:

$$\frac{u \Delta t}{\Delta x} + \frac{2 D \Delta t}{\Delta x^2} \leq 1$$

Well condition:

This condition says that the solute mass extracted at a sink node must be less or equal to the solute mass present in the respective grid cell. Looking on source nodes it says that the final solute concentration at the node must not exceed the concentration of the injected water:

$$Q c \Delta t = \Delta c B m \Delta x n_e$$

Transformation yields:

$$\frac{Q \Delta t}{B m \Delta x n_e} = \frac{\Delta c}{c} \leq 1$$

Assuming that the solute flux into the grid cell is equally distributed over both sides, $Q = 2qBm$, and with $q/n_e = u$ we can write:

$$\frac{2u \Delta t}{\Delta x} = 2Co \leq 1$$

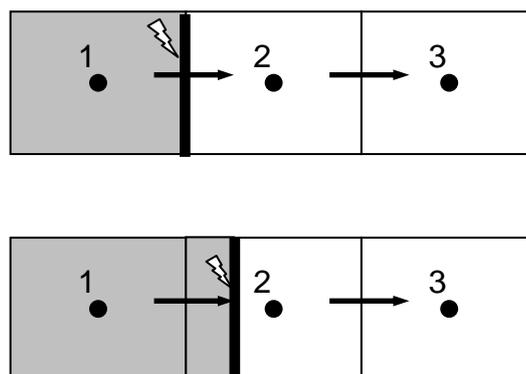
This condition means that the maximum allowable Courant number should be reduced from 1 to 0.5 if sink or source nodes are present in the model. The reason for this further restriction is that solute flux may enter a sink node from both sides, while unidirectional flow is assumed for the standard Courant condition. In a 3-dimensional application, the fluxes may enter or leave a sink/source cells over all 6 sides. Consequently the maximum Courant number can be as low as 1/6 in the 3-dimensional case.

Using an implicit scheme allows to partly violate the above mentioned conditions, i.e. it allows for generally larger time steps. However, observing the stability conditions is still recommended as it enhances the numerical accuracy.

Numerical accuracy

As mentioned before, the transport equation is of mixed parabolic (diffusion/dispersion) and hyperbolic (advection) type.

However, grid methods like the finite difference and the finite element method are especially suited for the solution of parabolic differential equations (e.g. the flow equation or the pure diffusive transport equation). The hyperbolic part of the transport equation leads in case of upwind-weighted differences to the so-called numerical dispersion. The following figure graphically illustrates this phenomenon:



A steep solute front leaves node 1 at time t driven by pure advective transport. After the time step Δt ($\Delta t < \Delta x/u$) the front will reach a certain position **in between** node 1 and node 2. Because of the discrete spacing part of the solute will already be assigned to node 2, i.e. the sharp solute front will become diffused in the model. This erroneous mixing is called numerical dispersion.

The contribution of numerical dispersion ∇_N to total mixing depends on the temporal differ-

ence schemes and was quantified by Herzer und Kinzelbach (1989). Spatial upwind weighting of differences was used in both cases:

$$\text{explicit scheme: } \alpha_N = \frac{1}{2}(\Delta x - u \Delta t)$$

$$\text{implicit scheme: } \alpha_N = \frac{1}{2}(\Delta x + u \Delta t)$$

For an implicit scheme numerical dispersion can be minimized by a fine spatial and temporal discretisation. An important criterion is the grid-Peclet number Pe_g :

$$Pe_x = \frac{u_x \Delta x}{D_{xx}}, Pe_y = \frac{u_y \Delta y}{D_{yy}}, Pe_z = \frac{u_z \Delta z}{D_{zz}}$$

Pe_g should always be less or equal to 2. Small grid-Peclet numbers ensure that the parabolic character of the differential equation prevails, i.e. that numerical dispersion effects become small compared to that of physical dispersion. For a given dispersivity \forall_1 the Peclet criterion provides the maximum recommended grid spacing.

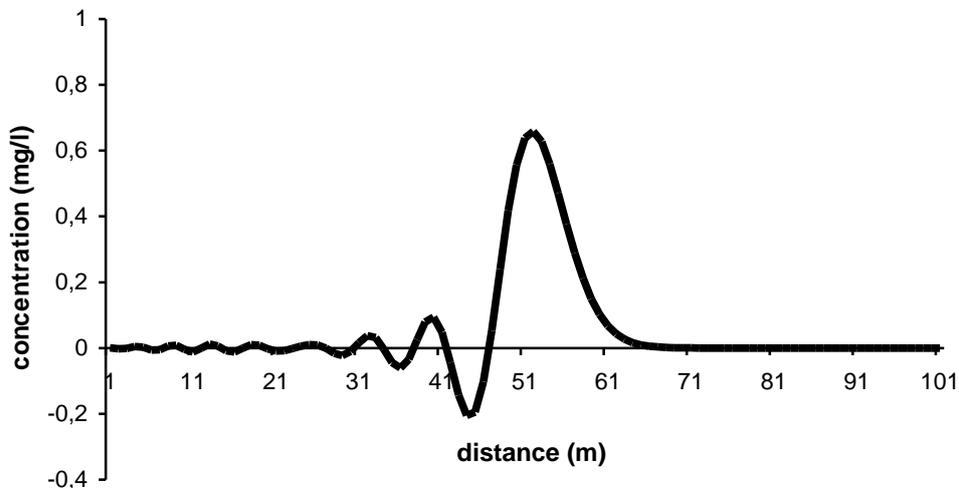
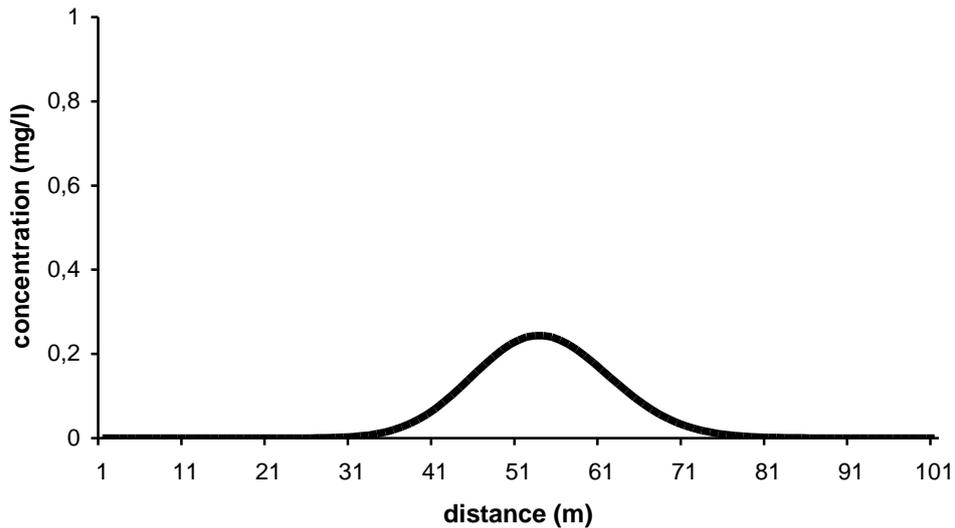
In an explicit scheme numerical dispersion can be eliminated by observing the condition:

$$u\Delta t = \Delta x$$

However, this is only possible in one-dimensional homogeneous models.

Another possibility to decrease the effects of numerical dispersion is to employ a central difference scheme in space. This drops the contribution of the grid spacing to numerical dispersion. However, central differences in space tend to produce numerical oscillations (“wiggles”).

The following figures demonstrate the effects of numerical dispersion and oscillations on solute transport. Simulated was the transport of a non-reactive solute in a one-dimensional domain. Dispersion was set to zero, i.e. a rectangular pulse should move through the hypothetical column if no numerical dispersion was active. The upper figure shows the result for a given time step when using an upwind-weighted difference scheme. Obviously there is a strong artificial mixing caused by numerical dispersion. The lower figure was generated using a central difference scheme. Here the effects from numerical dispersion are less pronounced, however appreciable oscillations have developed during the simulations.



According to the spatial discretisation scheme numerical dispersion and spurious oscillations emerge complementarily to each other. Both are expressions of an inappropriate discretisation. In general the effects of numerical dispersion and oscillations can be kept small if the grid-Peclet criterion is fulfilled ($Pe_g \# 2$). Furthermore the Courant criterion should be fulfilled for implicit schemes also ($Co \# 1$).

Basically central schemes are more accurate than upwind-weighted schemes. Furthermore inappropriate discretisation can be better recognized by the occurrence of oscillations than by that of numerical dispersion ("don't suppress the wiggles"). However, negative concentrations as a consequence of numerical oscillations may lead to serious problems if transport models

are coupled to chemical reaction models.

Numerical dispersion, which leads to an erroneously increased longitudinal mixing in the one-dimensional case may additionally produce an increased **transverse mixing** in two dimensions, if flow is not oriented parallel to one of the axis. For an extreme anisotropy of dispersivity ($\nabla_l/\nabla_t \gg 10$) observing the Courant- and Peclet condition is not sufficient to minimize the effects of numerical dispersion. Instead it is necessary to additionally consider transverse dispersion. For an explicit difference scheme with upwind-weighting the maximum grid spacing in the worst case ($u_x = u_y$) should be:

$$\Delta x = \Delta y < 2\sqrt{2} \alpha_t$$

In general a solute plume should be resolved by at least 10 nodes in transverse direction in finite difference methods. In many real field cases it will not be possible to achieve flow direction parallel to the grid everywhere in the model domain. Therefore the risk of excessive transverse dispersion is large in FD methods.

The three-dimensional transport with MT3D and MT3DMS

Completely new features do not arise for the transition from 2- to 3-dimensional transport. Accordingly the FD method derived for the 2-dimensional case can be directly transferred to 3 spatial dimensions. However, some particularities of the FD method as it is implemented in MT3D/MT3DMS are shown in the following.

In the isotropic case, the dispersion tensor is determined after Bear (1979):

$$D_{xx} = \alpha_l \frac{u_x^2}{u} + \alpha_t \frac{u_y^2 + u_z^2}{u} + D_m$$

$$D_{yy} = \alpha_l \frac{u_y^2}{u} + \alpha_t \frac{u_x^2 + u_z^2}{u} + D_m$$

$$D_{zz} = \alpha_l \frac{u_z^2}{u} + \alpha_t \frac{u_x^2 + u_y^2}{u} + D_m$$

$$D_{xy} = D_{yx} = (\alpha_l - \alpha_t) \frac{u_x u_y}{u}$$

$$D_{xz} = D_{zx} = (\alpha_l - \alpha_t) \frac{u_x u_z}{u}$$

$$D_{yz} = D_{zy} = (\alpha_l - \alpha_t) \frac{u_y u_z}{u}$$

with

$$u = |u| = \sqrt{u_x^2 + u_y^2 + u_z^2}$$

The tensor as it is developed above is exact in the isotropic case. In an anisotropic aquifer with different transverse dispersivities in horizontal and vertical direction, α_{th} and α_{tv} , MT3D/MT3DMS employs the approximation given by Burnett and Frind (1987):

$$D_{xx} = \alpha_l \frac{u_x^2}{u} + \frac{\alpha_{th} u_y^2 + \alpha_{tv} u_z^2}{u} + D_m$$

$$D_{yy} = \alpha_l \frac{u_y^2}{u} + \frac{\alpha_{th} u_x^2 + \alpha_{tv} u_z^2}{u} + D_m$$

$$D_{zz} = \alpha_l \frac{u_z^2}{u} + \frac{\alpha_{tv} u_x^2 + \alpha_{tv} u_y^2}{u} + D_m$$

$$D_{xy} = D_{yx} = (\alpha_l - \alpha_{th}) \frac{u_x u_y}{u}$$

$$D_{xz} = D_{zx} = (\alpha_l - \alpha_{tv}) \frac{u_x u_z}{u}$$

$$D_{yz} = D_{zy} = (\alpha_l - \alpha_{tv}) \frac{u_y u_z}{u}$$

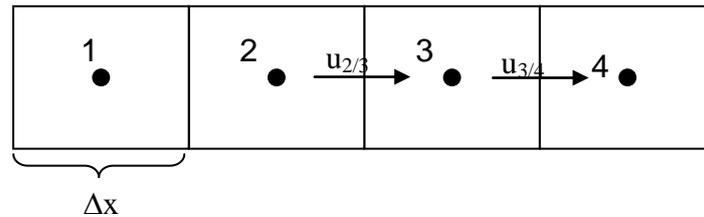
The time step size may be either specified by the user, or it can be set automatically by the program such that a given Courant number is not exceeded in the whole model domain. Advection, dispersion and source/sink cells are considered during automatic time step selection. A Courant number less than 1 has to be provided when using an explicit scheme ($0.2 < Co < 0.75$).

Prior to simulating solute transport flow calculations have to be performed with MODFLOW. This implies that any change in hydraulic parameters like e.g. pumping rates requires a new flow simulation before the new transport simulations is done.

The TVD method

TVD stands for TOTAL VARIATION DIMINISHING. All TVD methods have in common that the sum of the concentration differences between adjacent nodes is constantly decreased during the simulation. The TVD method implemented in MT3DMS is based on a third order FD method. Therefore it belongs to the Eulerian methods, i.e. a fixed grid is used.

A third order FD method means that a third order polynomial is employed to approximate the concentrations on a certain x/y/z-position in the model domain. To illustrate this scheme we consider a hypothetical one-dimensional model column consisting of four nodes:



The velocity u is constant and directed from left to right, the discretisation is Δx for all four nodes. For calculation of the advective transport from node 2 to node 3 one has to multiply the velocity $u_{2/3}$ with the concentration $c_{2/3}$. While $u_{2/3}$ is directly known from flow simulation ($u_{2/3} = -\frac{k_f}{n_e} \frac{h_3 - h_2}{\Delta x}$), the concentration $c_{2/3}$ is not known directly and has therefore to be interpolated from known adjacent concentrations. In the FD method shown before c_2 (upwind) or $(c_2 + c_3)/2$ (central weighting) have been used as approximations. The third order TVD method implemented in MT3DMS uses the following algorithm to interpolate $c_{2/3}$:

$$c_{2/3} = \frac{c_2 + c_3}{2} + Co \frac{c_2 - c_3}{2} - (1 - Co^2) \frac{c_1 - 2c_2 + c_3}{6}$$

with Co being the Courant-number ($Co = \frac{u\Delta t}{\Delta x}$).

The calculations for the advective transport from node 3 to node 4 is done with the same scheme. Finally the concentrations from nodes 1, 2, 3, and 4 are necessary for the formulation of the advective term for node 3.

MT3DMS utilizes an explicit scheme with the TVD method, i.e. the concentrations in the above equation are all taken from the previous simulation time. That means that the Courant criterion has to be strictly obeyed when using the TVD method. This is always guaranteed in MT3DMS as the time step is calculated internally according to the Courant restrictions. Dispersive transport and the reaction and source/sink terms are calculated with the implicit FD

method described before. For the realization of this approach in MT3DMS first the advective transport is simulated using the TVD scheme. Then the concentration changes caused by pure advective transport enters the subsequent dispersive transport calculations in form of an explicit source/sink term.

Similar to the central weighted FD method the TVD scheme as described above might lead to appreciable spurious oscillations in the vicinity of steep concentration gradients. To overcome this problem a so-called “flux limiter” is introduced. This limiter checks whether the interpolated concentrations on the interface of the nodes lie in between the range of the concentrations values of the respective adjacent nodes. For the example shown above it must hold that $c_2 < c_{2/3} < c_3$ if $c_2 < c_3$. If this is not the case, then the initial estimate for $c_{2/3}$ is replaced by the concentrations of the upstream node, c_2 . In other words, the flux limiter results in the replacement of the third order TVD scheme by a simple upwind weighted FD scheme if oscillations occur.

In general the solution of the transport equation is more accurate using the TVD scheme than using upwind or central weighted FD methods. However, also the numerical effort increases appreciably, caused by the more costly interpolation of the concentrations between the nodes and by the checking and eventual corrections by the flux limiter. Numerical dispersion is reduced by the TVD scheme, but it is not completely eliminated. This will only be achieved with the characteristics method presented in the next chapter.

MOC (METHOD OF CHARACTERISTICS)

Together with the following two methods (MMOC and HMOC) the MOC belongs to the group of mixed Eulerian-Lagrangian methods. Here the advective transport is simulated with a particle tracking procedure, while dispersive transport and reactions and sources/sinks are simulated with the standard FD method.

At the beginning of the advective transport calculations with the MOC virtual particles are distributed over the model domain. In the vicinity of concentration gradients it is necessary to place more than one particle per model cell, i.e. the particle number might become large for large 3D model domains. The user decides whether the particles are distributed randomly or whether they follow some fixed patterns. By this a position in the grid and a concentration C_p is attributed to each particle. The initial concentrations of the particle follow from the initial concentrations specified for the individual model cells. In MT3D/MT3DMS the grid for the transport calculations is adopted from the flow model.

In the next step the particles are moved by advection for one time step along the path lines derived from the flow simulations (“forward tracking” or “front tracking”). This technique requires the interpolation of the velocities for any position of the model domain from the known discrete velocities determined during flow simulation. MT3D/MT3DMS employs an stepwise interpolation scheme. This means that for instance the x-velocity for a given location in a cell is interpolated from the two known x-velocities at the interfaces of the cell.

In a linear interpolation scheme the known velocities are weighted according to their distance to the location under consideration:

$$q_x(x_p, y_p, z_p) = (1 - \alpha_x)q_{i,j-1/2,k} + \alpha_x q_{i,j+1/2,k}$$

with q_x = required Darcy velocity in x-direction

x_p, y_p, z_p = particle position in x, y, z-coordinates

$q_{i,j-1/2,k}, q_{i,j+1/2,k}$ = known Darcy velocity in x-direction at the two cell interfaces

α_x = weighting factor in x-direction = $(x_p - x_{j-1/2})/\Delta x_j$

Δx_j = grid spacing in x-direction

The same scheme is applied to y- and z-directions. Afterwards the pore velocities, which are the relevant parameters for advective transport, are determined from the Darcy velocities by

dividing them by the effective porosity. Finally the advective displacement of a particle results from the superposition of the individual displacements in the three spatial directions $\Delta x_p, \Delta y_p, \Delta z_p$:

$$\Delta x_p = u_x(x_p, y_p, z_p)\Delta t$$

$$\Delta y_p = u_y(x_p, y_p, z_p)\Delta t$$

$$\Delta z_p = u_z(x_p, y_p, z_p)\Delta t$$

Particle displacement in MT3D/MT3DMS may either be calculated with the simple linear scheme shown before or with a more costly but also more accurate fourth order Runge-Kutta scheme.

At the end of the advective part of the simulation the mean concentration is determined for each cell. The MOC implemented in MT3D/MT3DMS employs the arithmetic mean of the concentrations of the individual particles. The new concentration at the end of the advective step, C_{ad} , is then taken to define the concentrations used for dispersive transport and chemical reactions calculations with the FD method:

$$C_{ad}^* = \omega C_{ad} + (1 - \omega)C(\Delta t)$$

ω is a weighting factor which can take values between 0.5 and 1, and $C(\Delta t)$ is the concentration in the cell at the previous time step. The temporal weighting is motivated by the consideration that in reality advection, dispersion, and reaction occur simultaneously, while they are artificially decoupled in the MOC. Therefore a concentration somewhere in between the value at the end of the advective step, C_{ad} , and the average of the old concentration and C_{ad} is selected for the calculation of the concentration changes caused by dispersion and reaction, ΔC_{dis} .

The new concentration in a cell after advection, dispersion, and reaction, $C(t+\Delta t)$, is determined by:

$$C(t + \Delta t) = C_{ad} + \Delta C_{dis}$$

Prior to the simulation of the next advective step the concentrations of the individual particles residing in a given cell with a certain mean concentration have to be updated, i.e. the concentration changes caused by dispersion and reaction, ΔC_{dis} , have to be assigned to the particles. If ΔC_{dis} is a positive value, it is simply added to the old concentrations of the particles:

$$C_p(t + \Delta t) = C_p(t) + \Delta C_{dis}$$

However, if ΔC_{dis} is negative and there coexist particles with high and low concentrations in one cell, then it might happen that the concentrations of the particles with low initial concen-

trations become negative. This is physically meaningless and has to be avoided. So if the concentrations of one or more particle become negative, then all particles in the cell are replaced by a new set of particles which are all assigned the mean cell concentration $C(t+\Delta t)$.

In order to limit the total number of particles and thus the storage demand and computational efforts, a so-called dynamic approach for particle distribution is employed in MT3D/MT3DMS. That means that the particles are not uniformly distributed over the model grid, but that their spatial density is adapted to the requirements of the simulated transport problem. The important criterion is the relative concentration gradient in certain vicinity of a cell $DCCELL_{i,j,k}$:

$$DCCELL_{i,j,k} = \frac{CMAX_{i,j,k} - CMIN_{i,j,k}}{CMAX - CMIN}$$

$CMAX_{i,j,k}$ and $CMIN_{i,j,k}$ are the maximum and minimum concentration resp. in the vicinity of the cell with the index i,j,k . $CMAX$ and $CMIN$ are the total maximum and minimum concentrations resp. in the whole model domain.

If the relative gradient $DCCELL$ is large at a certain location in the model domain, then an increased number of particles are set there in order to allow for an accurate transport simulation in this region. On the other hand it is sufficient to resolve solute transport with fewer particles in regions with low relative concentration gradients $DCCELL$. For the typical case of a pollutant plume in an otherwise uncontaminated aquifer the dynamic approach allows to concentrate the particles mainly in the contaminated regions. By this the total number of particles is reduced compared to a homogeneous distribution, while the desired accurate simulation of the advective transport in the plume area is still ensured.

The dynamic approach is not only applied for initial particle distribution, but it helps to optimize particle distributions throughout the whole simulation. Adapting the particle distribution is for instance required in cells with sources or sinks. Here it must be warranted that new particles are continuously set in source cells (e.g. inflow boundaries) such that the particle number does not fall below a given threshold, while particles are removed in sink cells (e.g. pumping wells) to avoid excessive particle numbers there. However, it might also be reasonable to adapt particle numbers in cells without sources or sinks, e.g. if the local concentration gradients change during the simulation.

The big advantage of the MOC is that is virtually free of numerical dispersion even for large

grid Peclet-numbers. The treatment of the advective transport with a particle tracking method ensures for instance that sharp concentration fronts are sustained independent of their relative position in the underlying grid. But despite the dynamic approach the storage requirements and the computational efforts might still be tremendous because of the large number of particles necessary especially in three-dimensional domains. The biggest disadvantage of the MOC compared to e.g. the FD method, however, consists in the fact that it is not mass conserving. Mass balance errors are the consequence of the permanent switching between particle tracking and the FD method during transport simulations. They are pronounced for irregular grids. The drawback of the inaccurate mass balance is especially important if non-linear chemical reactions have to be considered in addition to advective and dispersive transport.

MMOC (MODIFIED METHOD OF CHARACTERISTICS)

While the movement of a large number of particles in a given flow field is tracked in the standard MOC, only one virtual particle is placed in the center of each cell for the MMOC. Then the theoretical starting positions x,y,z of these particles to reach the center of each cell are calculated (backward tracking). Finally the known concentrations at the starting positions from the previous time step $C(\Delta t, x,y,z)$ are used as new concentrations for the cells at the end of the advective transport step $C_{ad}(t+\Delta t, K)$:

$$C_{ad}(t + \Delta t, K) = C(\Delta t, x, y, z)$$

In general the starting position x,y,z will not coincide with the location of a node, i.e. the concentration at the starting position will not be known and has to be interpolated from the known concentrations of the adjacent nodes. MT3D/MT3DMS employs a linear (tri-linear in 3D) interpolation scheme, where the concentrations of the adjacent nodes are weighted proportionate to their distance to the starting position x,y,z (8 neighboring nodes are considered in 3D). For the scheme presented below it is assumed that the starting position x,y,z lies between x_j and x_{j-1} , y_j and y_{j-1} , and z_j and z_{j-1} :

$$\begin{aligned} C(\Delta t, x, y, z) = & (1-\alpha_x)(1-\alpha_y)(1-\alpha_z)C_{i-1,j-1,k-1} + (1-\alpha_x)\alpha_y(1-\alpha_z)C_{i,j-1,k-1} \\ & + \alpha_x(1-\alpha_y)(1-\alpha_z)C_{i-1,j,k-1} + \alpha_x\alpha_y(1-\alpha_z)C_{i,j,k-1} \\ & + (1-\alpha_x)(1-\alpha_y)\alpha_z C_{i-1,j-1,k} + (1-\alpha_x)\alpha_y\alpha_z C_{i,j-1,k} \\ & + \alpha_x(1-\alpha_y)\alpha_z C_{i-1,j,k} + \alpha_x\alpha_y\alpha_z C_{i,j,k} \end{aligned}$$

$$\text{with } \alpha_x = \frac{x - x_{j-1}}{\Delta x}$$

$$\alpha_y = \frac{y - y_{j-1}}{\Delta y}$$

$$\alpha_z = \frac{z - z_{j-1}}{\Delta z}$$

x, y and z denote the x -, y - und z -position of the starting location. The variable grid distances

have to be considered during the determination of the weighting factors for irregular grids.

The subsequent steps, i.e. the calculation of concentration changes caused by dispersion and reaction, are similar to the procedures exemplified for the MOC.

Problems with the MMOC might arise in cells with sources and sinks. Therefore special particle distributions are employed for cells of this type.

The reduced number of particles used in the MMOC compared to the MOC results in reduced storage requirements and reduced computational efforts. However, a certain numerical dispersion is introduced to the method by the linear concentration interpolation used to determine the concentration values at the starting positions x,y,z . By this the MMOC partly loses the big advantage of the MOC compared to the FD method.

Theoretically one could utilize a higher order interpolation scheme to reduce numerical dispersion. However, this would also imply an increased computational effort, and spurious oscillations could arise. MT3D/MT3DMS provides only a linear interpolation scheme.

HMOC (HYBRID METHOD OF CHARACTERISTICS)

This method is a combination of MOC and MMOC. The HMOC merges the advantages of the two previously described methods in that it uses MOC or MMOC according to the requirements of the simulated transport problem. The MOC is always used for sharp solute fronts and thus for steep concentration gradients, as numerical dispersion will especially arise in such regions. An increased computational effort is accepted here. The less costly MMOC is employed outside regions with solute fronts, where concentration gradients are relatively low. If an initially sharp front is gradually diffused by dispersion or reaction during simulations, then the HMOC automatically switches from MOC to MMOC.

The criterion for switching between the two methods is the local relative concentration gradient DCCELL (remember that this criterion was also used to adapt particle distribution in the dynamic approach of the MOC). If DCCELL exceeds a certain threshold value defined by the user then MOC is used or the method switches from MMOC to MOC. On the other hand MMOC is used or MOC is switched to MMOC for low values of DCCELL. Switching requires that either additional particles are set (MMOC \rightarrow MOC) or that existing particles are partly removed (MOC \rightarrow MMOC). The appropriate method is checked for each cell and for each time step.

The HMOC allows for an accurate simulation with a limited number of particles. Therefore it should be able to completely replace the two underlying methods (MOC and MMOC). In practice however, automatic switching does not always lead to the expected results, and it might be desirable to use exclusively either one of the basic methods MOC and MMOC. Therefore all 3 methods are offered by MT3D/MT3DMS.

Comparison of the methods

Unfortunately none of the simulation methods described before is superior to all others and under all circumstances. In fact the question concerning the optimal method has to be answered problem-specific. Thus different methods might prove to be most appropriate for different model situations according to the boundary conditions, computer performance, and requirements to the results. Although the user will most probably develop certain preferences during practical experience with simulations, one of the great virtues of MT3D/MT3DMS is that it offers an appreciable variety of simulation methods to the user.

In the following some assets and drawbacks of the individual methods are compiled in tabular form.

	FD explicit	FD implicit	TVD	MOC	MMOC	HMOC
computational effort or storage demand	low	medium	large	large	low	large
numerical dispersion or oscillations	large	large	small	null	medium	small
mass balance	exact	exact	exact	not exact	not exact	not exact
maximum time step	small	large	small	large	large	large

The following compilation provides recommendations for typical transport problems in groundwater. Of course these recommendations are not meant to be universally valid, but they are rather rough orientation guides.

Characteristics of the model application	Recommended method
Pronounced spatial concentration gradients (e.g. contaminant plume with point source, lab study with contaminant pulse)	TVD, MOC, HMOC
Regional scale contaminant transport with small concentration gradients (e.g. nitrate transport with distributed sources)	FD
Exact mass balance important (e.g. coupling of transport and non-linear reactions)	TD, TVD
Large time steps required (e.g. long range solute transport over decades)	FD implicit, HMOC
Large grid Peclet numbers (small dispersivities or large grid spacing)	MOC, HMOC

Exercise on transport modeling using MT3DMS and PMWIN

Contaminant transport has to be simulated for a three-dimensional part of a hypothetical aquifer

Flow

First groundwater flow has to be calculated:

The model domain consists of 5 layers, 51 cells in x-direction (columns) and 21 cells in y-direction (rows) (i.e. the total number of nodes is 5355).

- Discretisation is 50 m and is constant in x- and y-direction ($\Delta x = \Delta y = 50$ m)
- The top layer is unconfined, the remaining four layers are always confined.
- A fixed head boundary has to be assumed on the left and right hand side of the model domain across the total thickness of the aquifer. The two other sides and the aquifer bottom are impermeable. (Remember that the model automatically assumes an impermeable boundary if not stated otherwise).
- The discretisation in z-direction is 10 m for all layers. The top of the aquifer is at $z = 105$ m (item "Top and Bottom of Layers"). Hence the total aquifer thickness is 50 m.
- Steady state groundwater flow can be assumed.
- The fixed head at the left hand side is $h = 100$ m, and at the right hand side $h = 97.5$ m. The resulting head gradient I is $2.5\text{m} / 2500\text{m} = 0.001$. The fixed heads have the same values in all layers
- The horizontal hydraulic conductivity k_{fh} is 10^{-3} m/s in layers 1, 2, 4 and 5, the vertical hydraulic conductivity there is $k_{\text{fv}} = 4 \times 10^{-4}$ m/s. This corresponds to an anisotropy factor $k_{\text{fh}}/k_{\text{fv}}$ of 2.5.
- Layer 3 has a reduced horizontal hydraulic conductivity of 10^{-4} m/s and a reduced vertical hydraulic conductivity of 4×10^{-5} m/s.
- The effective porosity is $n_e = 0.3$ anywhere in the model domain.
- Groundwater recharge in the whole model area is 200 mm/a or 6.3×10^{-9} m/s.
- A pumping well is located in the cell with the coordinates $x=35$, $y=11$, $z=5$. The pumping rate is -0.015 m³/s.
- Select the PCG2 method (preconditioned conjugate gradients) with "Modified Incomplete Cholesky" – preconditioning as solution method. The maximum number of inner iterations is 30 and that of the outer iterations is 50. The maximum allowable difference in heads between 2 iterations is 10^{-5} m, the difference in water flux 10^{-5} m³/s.

Please simulate groundwater flow and illustrate the calculated head distributions for layers 1 and 5. How can the difference between the two layers be explained?

Transport:

§ An idealized rectangular contaminant source is located in the cells (20/8), (20/9), (21/8) and (21/9). This spill area represents a permanent contaminant source. All groundwater passing by the spill adopts a contaminant concentration of 1000 g/m^3 . The spill area is limited to the top layer of the aquifer.

Please illustrate advective contaminant transport with the help of pathlines. Will the well be affected by the groundwater contamination?

- Two virtual observation points have to be installed in order to trace contaminant spreading. One of them is located directly in the well (lowest layer), the other is located at a distance of about 150 m away from the well in the top layer (coordinates $x = 35$, $y = 8$, $z = 1$).
- Contaminant transport has to be simulated for a period of 20 years ($= 6.28 \times 10^8 \text{ s}$). Please use the MT3DMS model and apply the 6 different transport methods one after the other:
 1. Finite difference method with upwind-weighting
 2. Finite difference method with central in space weighting
 3. Total Variation Diminishing method (TVD)
 4. Method of Characteristics (MOC)
 5. Modified Method of Characteristics (MMOC)
 6. Hybrid Method of Characteristics (HMOC)

§ Longitudinal dispersivity α_1 is 10 m. The resulting grid Peclet number in x-direction Pe_{gx} is $\Delta x/\alpha_1 = 5$. The horizontal transverse dispersivity 1 m, the vertical transverse dispersivity is 0.1 m.

Display the breakthrough curves for the two observation points for 20 years of simulation. Discuss the differences between the two curves.

Warning: Output times have to be specified in the „Output Control“ item. A meaningful value for NPRS („output frequency“) is 11 or larger.

What looks the contaminant distribution like in layers 1 and 5 after 20 years? How is the position of maximum contamination shifted along the pollutant plume in the different layers? What would the contaminant distribution look like if the well was not in operation? Store the graphical illustrations of the concentration distribution in DXF-format.

Input parameters for the different simulation methods

FD upwind:

Courant number (PERCEL):	0.75
Solver:	GCG (General Conjugate Gradient)
Preconditioning Method:	Jacobi
Max. Number of Outer Iterations (MXITER):	1
Max. Number of Inner Iterations (ITER1):	50
Relaxation Factor:	1
Concentration Closure Criterion:	0.000001
Concentration Change Printout Interval:	0
Do not include full dispersion tensor	

FD central:

Same parameters as for FD upwind

TVD:

All parameters are set automatically (e.g. via stability criteria)

MOC:

Particle Tracking Algorithm: Hybrid 1st order Euler and 4th order Runge-Kutta

Simulation Parameters:

Max. number of total moving particles (MXPART):	50000
Courant number (PERCEL):	0.75
Concentration weighting factor (WD):	0.5
Negligible relative concentration gradient (DCEPS):	0.00001
Pattern for initial placement of particles (NPLANE):	4
No. of particles per cell in case of $DCCELL \leq DCEPS$ (NPL):	0
No. of particles per cell in case of $DCCELL > DCEPS$ (NPH):	30
Minimum number of particles allowed per cell (NPMIN):	0
Maximum number of particles allowed per cell (NPMAX):	40

MMOC:

Particle Tracking Algorithm: Hybrid 1st order Euler and 4th order Runge-Kutta

Simulation Parameters:

Courant number (PERCEL):	0.75
Concentration weighting factor (WD):	0.5
Negligible relative concentration gradient (DCEPS):	0.00001
Pattern for placement of particles for sink cells (NLSINK):	0
No. of particles used to approximate sink cells (NPSINK):	30

HMOC:

Particle Tracking Algorithm: Hybrid 1st order Euler and 4th order Runge-Kutta

Simulation Parameters:

Max. number of total moving particles (MXPART):	50000
Courant number (PERCEL):	0.75
Concentration weighting factor (WD):	0.5
Negligible relative concentration gradient (DCEPS):	0.00001
Pattern for initial placement of particles (NPLANE):	4
No. of particles per cell in case of DCCELL<=DCEPS (NPL):	0
No. of particles per cell in case of DCCELL>DCEPS (NPH):	30
Minimum number of particles allowed per cell (NPMIN):	0
Maximum number of particles allowed per cell (NPMAX):	40
Pattern for placement of particles for sink cells (NLSINK):	0
No. of particles used to approximate sink cells (NPSINK):	30
Critical relative concentration gradient (DCHMOC):	0.0001

Transport and reaction

So far we have considered the transport of non-reactive solutes only. However, most solutes are subject to reactive processes in addition to advection and diffusion/dispersion in the aquifer. For instance cations may adsorb onto clay minerals or other negatively charged surfaces and many organic compounds are affected by microbially mediated degradation. A non-reactive behavior can be assumed for a few solutes only, e.g. for chloride or for uranin (organic dye). There are many model approaches of different complexity to account for reactive processes in aquifers. Two rather simple and widely used examples are first order degradation and linear retardation.

First order degradation

First order degradation means that the temporal concentration change of a solute is proportional to the actual concentration c itself. The proportionality factor is the degradation rate λ :

$$\frac{dc}{dt} = -\lambda c$$

This ordinary differential equation can be easily integrated:

$$\frac{1}{c} dc = -\lambda dt$$

$$\int_{c_0}^c \frac{1}{c} dc = \int_{t_0}^t -\lambda dt$$

$$\ln c - \ln c_0 = \ln \frac{c}{c_0} = -\lambda t \quad (t_0 = 0)$$

$$\frac{c}{c_0} = e^{-\lambda t} \quad \text{or} \quad c = c_0 e^{-\lambda t}$$

with c = concentration [M L^{-3}]

t = time [T]

λ = degradation rate [T^{-1}]

A well known process that can be macroscopically described with a first order law is the radioactive decay of a substance. Under certain circumstances the first order law can also be used to describe the chemical or biochemical degradation of a solute. For instance if the degradation rate of a contaminant depends on its own concentration only, i.e. if the concentrations of other substances involved in the reactions like e.g. oxidants are not rate limiting, then contaminant degradation may be described by a first order law.

A first order degradation term is considered in most standard groundwater transport models. It may be used if it becomes obvious that the solute under consideration disappears in the model domain. Furthermore so-called biochemical half-lives are documented for many common organic compounds. This half-lives haven been determined in laboratory and field studies and are a rough estimate for the degradation behavior of a solute in a given environment (e.g. aerobic or anaerobic conditions). The degradation rate can be directly determined from the half-life $t_{1/2}$:

$$c(t = t_{1/2}) = \frac{c_0}{2}$$

$$\frac{c_0}{2} = c_0 e^{-\lambda t_{1/2}}$$

$$\frac{1}{2} = e^{-\lambda t_{1/2}}$$

$$\ln\left(\frac{1}{2}\right) = -\lambda t_{1/2}$$

$$-\ln 2 = -\lambda t_{1/2}$$

$$\lambda = \frac{\ln 2}{t_{1/2}}$$

Retardation

The retardation of a solute is caused by its interaction with the aquifer material. Different types of interactions are summarized by the term adsorption or sorption. The implementation of linear retardation in a transport model is exemplified for the one-dimensional transport equation with constant porosity and without additional sinks/sources:

$$1. \quad n_e \frac{\partial c_g}{\partial t} = -n_e u \nabla c_g + n_e \nabla (D \nabla c_g) + S_1$$

$$2. \quad \rho_{mat} n_{mat} \frac{\partial c_a}{\partial t} = S_2$$

with n_e = effective porosity [-]

n_{mat} = specific volume of the aquifer material [-]

Δ_{mat} = density of the aquifer material (usually 2.5 -2.65 kg l⁻¹) [M L⁻³]

c_g = concentration of the species in the pore water [M L⁻³]

c_a = concentration of the species adsorbed to the aquifer material [M M⁻¹]

S_1, S_2 = source/sink terms

Mass conservation requires that $S_1 = -S_2$. Both equations can be combined into one equation:

$$n_e \frac{\partial c_g}{\partial t} = -n_e u \nabla c_g + n_e \nabla (D \nabla c_g) - \rho_{mat} n_{mat} \frac{\partial c_a}{\partial t}$$

or

$$n_e \frac{\partial c_g}{\partial t} + \rho_{mat} n_{mat} \frac{\partial c_a}{\partial t} = -n_e u \nabla c_g + n_e \nabla (D \nabla c_g)$$

In case of linear retardation the correlation between dissolved and adsorbed concentration is given by a linear isotherm:

$$c_a = k_d c_g$$

with k_d = adsorption coefficient or distribution coefficient or partitioning coefficient [L³ M⁻¹]

Using k_d the above equation may be further transformed:

$$n_e \frac{\partial c_g}{\partial t} + \rho_{mat} n_{mat} k_d \frac{\partial c_g}{\partial t} = -n_e u \nabla c_g + n_e \nabla (D \nabla c_g)$$

$$\frac{\partial c_g}{\partial t} + \frac{\rho_{mat} n_{mat} k_d}{n_e} \frac{\partial c_g}{\partial t} = -u \nabla c_g + \nabla (D \nabla c_g)$$

$$\frac{\partial c_g}{\partial t} \left(1 + \frac{\rho_{mat} n_{mat} k_d}{n_e} \right) = -u \nabla c_g + \nabla (D \nabla c_g)$$

Now it is possible to define the so-called retardation factor R:

$$R = \left(1 + \frac{\rho_{mat} n_{mat} k_d}{n_e} \right)$$

Using R the conventional notation can be obtained:

$$R \frac{\partial c_g}{\partial t} = -u \nabla c_g + \nabla (D \nabla c_g)$$

or

$$\frac{\partial c_g}{\partial t} = -\frac{u}{R} \nabla c_g + \frac{1}{R} \nabla (D \nabla c_g)$$

$\Delta_{mat} n_{mat}$ is often combined to the bulk density Δ_b . n_{mat} can be expressed by $1 - n$ with n being the total (geometric) porosity of the medium

The retardation factor R is usually greater than 1, i.e. the transport of the respective solute is delayed compared to the mean water movement by a factor of R. Organic solutes will always experience a certain amount of retardation. For these substances empirical relations have been established between certain physico-chemical properties of the substance and the retardation factor. The most frequently used compound property is its distribution coefficient between octanol (an alcohol with 8 C-atoms) and water k_{ow} . The k_{ow} is a measure of the polarity of a given compound. The higher its value, the less polar or lipophilic a compound is, and the higher is its tendency to leave the polar water phase and to adsorb to the less polar constituents of the aquifer material.

For different groups of compounds correlations could be found in laboratory studies between the k_{ow} of a substance and its distribution coefficient between natural organic aquifer material (e.g. humic substances) and water (k_{oc}). Some examples are:

1.)

$$k_{oc} = 0.63 k_{ow}$$

2.)

$$k_{OC} = 9.92 k_{OW}^{0.54}$$

3.)

$$k_{OC} = 3.09 k_{OW}^{0.72}$$

with k_{oc} in $L\ kg^{-1}$

Equation 1) is valid for hydrophobic aromatic hydrocarbons (Karickhoff et al., 1979), equation 2) for halogenated hydrocarbons (Briggs, 1981) and equation 3) for tetrachloroethylene and chlorinated benzenes (Schwarzenbach und Westall, 1981).

The k_{OC} 's refer to natural organic carbon. The k_D of a substance is obtained by multiplying the k_{OC} with the fractional organic carbon content of the aquifer f_{OC} :

$$k_D = f_{OC} k_{OC}$$

The empirical relations are applicable for $f_{OC} > 0.001$ only. For a lower content of natural organic carbon interactions of the organic solutes with minerals, especially clay minerals, can no longer be neglected.

- The following table shows calculated retardation factors for some typical contaminants in a hypothetical aquifer with $n_e = 0.3$, $n_{mat} = 0.7$, $\Delta_{mat} = 2.65\ kg/l$ and $f_{OC} = 0.001$. The k_{OC} values are taken from Montgomery und Welkom (Groundwater Chemicals Desk Reference):

substance	usage	formula	k_{OC} [L/kg]	R [-]
tetrachloroethene (PER)	solvent	C_2Cl_4	250	2.55
vinyl chloride	intermediate	C_2H_3Cl	2.5	1.02
benzene	fuel additive	C_6H_6	60	1.37
o-xylene	solvent	C_8H_{10}	130	1.8
monochlorobenzene	pesticide production	C_6H_5Cl	310	2.9
1,2,4-trichlorobenzene	pesticide production	$C_6H_3Cl_3$	1600	10.9
hexachlorocyclohexan (Lindan)	pesticide	C_6Cl_6	1900	12.75

Besides linear isotherms it is also possible to use adsorption models with non-linear isotherms, e.g.:

- Freundlich isotherm:

$$c_a = k c_g^n$$

with k = Freundlich constant [dimension depends on n]

n = Freundlich exponent [-]

The linear isotherm can be considered as a special case of the Freundlich isotherm with $n = 1$. For $n < 1$ the solute is preferentially adsorbed for lower dissolved concentrations (convex isotherm), while preferential adsorption for higher solute concentrations is realized with $n > 1$ (concave isotherm).

- Langmuir isotherm:

$$c_a = \frac{c_{a,\max} k_L c_g}{1 + k_L c_g}$$

with k_L = Langmuir constant [$L^3 M^{-1}$]

$c_{a,\max}$ = maximum adsorbed concentration (saturation concentration) [$M M^{-1}$]

The Langmuir isotherm is a so-called saturation isotherm. The denominator approaches 1 for low dissolved concentrations c_g , i.e. a nearly linear adsorption behaviour arises. For high c_g the adsorbed concentration c_a approaches the maximum adsorbed concentration $c_{a,\max}$ and effects of adsorption on solute transport decrease.

Generally the different isotherms link dissolved and adsorbed concentrations:

$$c_a = f(c_g)$$

Therefore it can be written more generally:

$$n_e \frac{\partial c_g}{\partial t} + \rho_{mat} n_{mat} \frac{\partial c_a}{\partial t} = n_e u \nabla c_g + n_e \nabla (D \nabla c_g)$$

$$n_e \frac{\partial c_g}{\partial t} + \rho_{mat} n_{mat} \frac{\partial f(c_g)}{\partial t} = n_e u \nabla c_g + n_e \nabla (D \nabla c_g)$$

$$n_e \frac{\partial c_g}{\partial t} + \rho_{mat} n_{mat} \frac{\partial f}{\partial c_g} \frac{\partial c_g}{\partial t} = n_e u \nabla c_g + n_e \nabla (D \nabla c_g)$$

$$\frac{\partial c_g}{\partial t} \left(1 + \frac{\rho_{mat} n_{mat}}{n_e} \frac{\partial f}{\partial c_g} \right) = n_e u \nabla c_g + n_e \nabla (D \nabla c_g)$$

R for the Freundlich isotherm is:

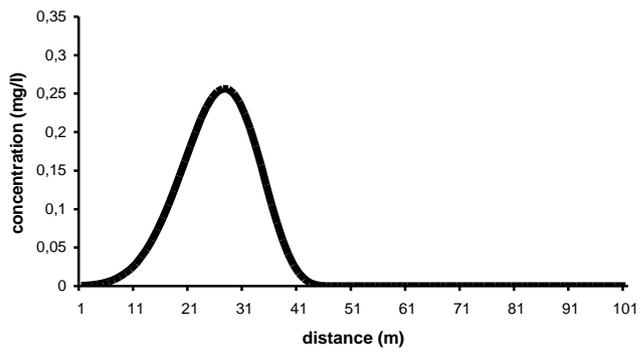
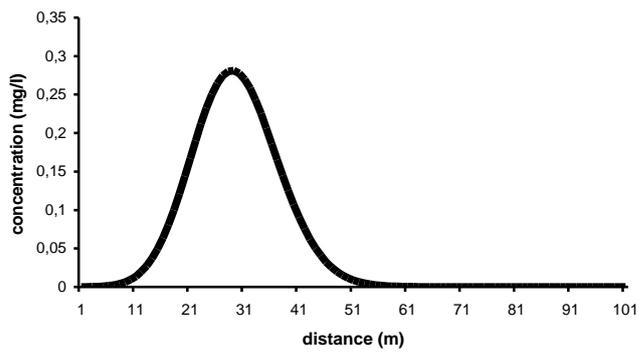
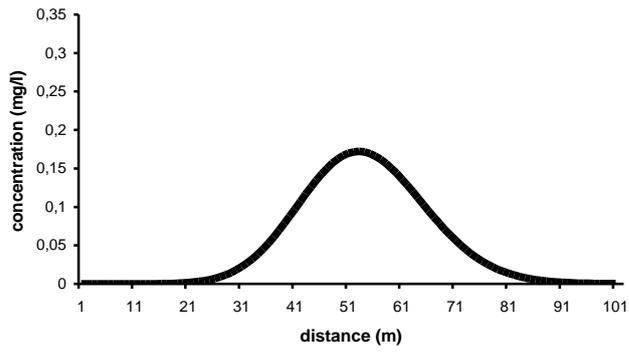
$$R_F = 1 + \frac{\rho_{mat} n_{mat}}{n_e} n k c_g^{n-1}$$

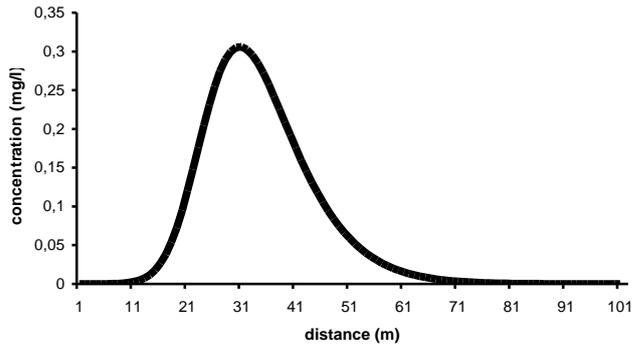
The following retardation factor is received for the Langmuir isotherm:

$$R_L = 1 + \frac{\rho_{mat} n_{mat}}{n_e} \frac{c_{a,max} k_L}{(1 + k_L c_g)^2}$$

The numerical solution of the transport equation with the standard methods requires the linearisation of non-linear isotherms. Therefore the retardation factors are treated explicitly, i.e. the dissolved concentrations c_g from the previous time step are used.

The following figures illustrate the impact of different isotherms on solute transport for a hypothetical one-dimensional situation. All concentration distributions are displayed for the same simulation time. The top figure shows solute spreading without any retardation ($R=1$). The figure below illustrates the effects of a linear isotherm with $R=2$. The third figure from top was generated using a Freundlich isotherm with an exponent of 0.8 (convex isotherm). The bottom figure exemplifies the impact of a Freundlich isotherm with an exponent of 1.3 (concave isotherm).





The following differential equations are solved in MT3D/MT3DMS for reactive transport simulations:

$$R \frac{\partial c}{\partial t} = -u \nabla c + \nabla(D \nabla c) + \frac{\sigma}{n_e} + \frac{w}{n_e} c_z - \lambda c$$

or

$$\frac{\partial c}{\partial t} = -\frac{u}{R} \nabla c + \frac{1}{R} \nabla(D \nabla c) + \frac{\sigma}{R n_e} + \frac{w}{R n_e} c_z - \frac{\lambda}{R} c$$

That means that the solution of the transport equations proceeds analogous to the non-reactive case, but now with an additional linear decay term and with all terms on the right hand side divided by R.

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