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1. Introduction

1.1. Classification of solutes, pollutants and subsurface pollution

Solute transport is of importance in view of the movement of nutrient elements, e.g., towards the plant root system, and because of a broad range of pollutants. Pollution of the subsurface is often considered to be either point source pollution or diffuse source pollution. Point source pollution covers a limited area, and is often caused by accidental (or illegal) spills (e.g., leaking pipes, tanks, mine tailings, etc.). Diffuse source pollution covers a large area and is in general caused by large-scale application of both beneficial and hazardous compounds at the soil surface (manure and fertilizer, pesticides, atmospheric deposition of acids and radio nuclides, etc.). Pollution is not necessarily man induced, but may be due to geological or geohydrological causes, e.g., in the cases of pollution with arsenic, and salt.

For the polluting species, a distinction can be made between dissolved and immiscible, and between conservative and reactive. Dissolved pollutants (aqueous phase pollutants) will spread with the groundwater due to groundwater flow, diffusion and dispersion. Immiscible pollutants will spread as a separate phase (non-aqueous phase liquids, NAPL). They will contain components with very low solubility in the water phase. They constitute a long-term source for pollution.

Conservative pollutants are those that do not react with the solid soil material, do not react with other pollutants and will not be degraded by biological activity. Reactive solutes may enter or leave the water phase through adsorption/desorption, chemical reactions, dissolution/precipitation and/or biodegradation.

1.2. Some basic definitions

Advection: the spreading of a pollutant by groundwater flow.
**Diffusion**: the spreading of a species dissolved in the water phase by the Brownian motion of the ions (molecules).

**Dispersion**: the spreading of a species dissolved in the water phase by local variations in the water velocity.

**Adsorption/desorption**: interaction of species dissolved in the water phase with the solid matrix. This process can be physically based or chemically based, reversible or irreversible.

**Chemical reactions**: reactions of species dissolved in the water phase with other species, resulting in the occurrence of different species altogether.

**Biodegradation**: the degradation of species dissolved in the water phase by bacteria.

**Radioactive decay**: the degradation of species by radioactivity.

Concentrations of species in the water phase \( C_i \) (including pure water itself) are defined as the mass of the species per unit volume: \( \text{kg/m}^3, \text{g/l}, \text{mg/l}, \text{etc.} \).

The density of a multi-component fluid, consisting of \( N \) components, is then given as:

\[
\rho = \sum_{i=1}^{N} C_i \tag{1}
\]

Mass fractions \( \omega \) of the components (mass per unit of mass: \( \text{kg/kg}, \text{g/g}, \text{etc.} \)) are defined as:

\[
\omega_i = \frac{C_i}{\rho} \quad \text{such that} \sum_{i=1}^{N} \omega_i = 1 \tag{2}
\]

For dilute solutions (tracer concentrations) all mass fractions \( \omega_i \ll 1 \), except for the pure water. This means that the density of the fluid is close to the density of pure water, and can be assumed to be constant.

Water density is a function of pressure, temperature and composition. This last dependence is only important at high concentrations. E.g. in case of seawater intrusion, or in deep saline aquifers which are sometimes used to store waste or to produce energy. In these deep aquifers salt concentrations can be as high as 300 g/l, resulting in a water density of 1200 g/l (giving a salt mass fraction of 0.25). Water density fluctuations will also play a role in the subsurface storage of heat.

Water viscosity is a function of pressure, temperature and composition. This influences the hydraulic conductivity (see next section). The dependence on the temperature is by far the most important. Hence, this dependence must be taken into account in the analysis of subsurface storage of heat.
modelling. For instance, the stochastic theory for water flow and solute transport resulted in equations for the macro dispersivities. However, these dispersivities do not necessarily represent real mixing. Briefly, this issue is discussed by both Janssen et al. (2006) and Eeman et al. (2012).

Whereas conventional solute transport often considered only one scale of heterogeneity (the grain or soil sample scale), the stochastic approach addressed so far mainly two scales, the microscopic and one larger scale, the last characterized by statistics of macroscopic properties such as the hydraulic conductivity or the retardation factor. In reality, we have to deal with a whole hierarchy of scales, from grain, to sample, horizon/layer, geological strata, to watershed. Comprehensive theory cannot address all these scales in a simple theory, so it considers those that are deemed most important.

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\[
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\]
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\[ \frac{C_{i+1}^n - C_{i-1}^n}{2D} = \frac{C_{i+1}^{n-1} - 2C_i^n + C_{i-1}^{n+1}}{D} \]

Consider the explicit finite difference approximation of the 1-dimensional solute transport equation, where the advective term has been approximated by a central difference:

\[ C_{i+1}^n - C_{i-1}^n \]

\[ + \frac{C_{i+1}^{n-1} - 2C_i^n + C_{i-1}^{n+1}}{D} \]

Solute Transport in Soil

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\[
\frac{C_i^{n+1} - C_i^n}{\Delta t} = D_n \frac{C_i^{n+1} - C_i^{n-1}}{2\Delta x} - D_s \frac{C_i^{n+1} - C_i^{n+1}}{2\Delta y} + \frac{Q_i}{k} \left( C_i^{n+1} - C_{i+1}^{n+1} \right)
\]

(125)

Solute Transport in Soil

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\[
C_{i+1} - C_{i} = \left[ \frac{1}{2} \left( C_{i+1} - C_{i} \right) \right] \Delta x + \frac{D}{\Delta t} \nabla^2 C_i
\]

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Solute Transport in Soil
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$$C_n + C_{n+1} + C_{n-1} - C_n = D_n C_{n+1} - D_{n-1} C_{n-1}$$

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\[
\begin{align*}
C(i+1, n) &= C(i, n) + D(\frac{C(i, n) - C(i-1, n)}{x} - \frac{C(i, n) - C(i, n-1)}{Dt}) + D(\frac{C(i, n) - C(i, n)}{x} - \frac{C(i, n) - C(i, n-1)}{Dt})
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$$\frac{C_{i+1}^n - C_i^n}{\Delta t} + \frac{C_{i+1}^{n+1} - C_{i-1}^{n+1}}{2\Delta x} + \frac{D_{i+1}^{n+1} - D_i^{n+1}}{\Delta t} = 0$$

(125)
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\[
\frac{C_{i}^{n+2} - 2C_{i}^{n+1} + C_{i}^{n}}{2Dt} + \frac{C_{i}^{n+1} - C_{i}^{n-1}}{2x} = D_{i}^{n+1} - D_{i}^{n-1}.
\]

(S125)
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Consider the explicit finite difference approximation of the 1-dimensional solute transport equation, where the advective term has been approximated by a central difference:

\[
C_i^{n+1} = C_i^n + \frac{D}{2} \left( \frac{C_{i+1}^{n} - C_{i-1}^{n}}{2\Delta x} \right) \Delta t
\]

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\[
\frac{C_{i+1} - C_i}{Dt} = D \frac{C_{i+1} - 2C_i + C_{i-1}}{x^2},
\]

where \( C \) is the solute concentration, \( Dt \) is the time step, and \( D \) is the dispersion coefficient.
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\[
C_{i+1} - C_i = -D_{i+1/2} - D_{i-1/2} \frac{\Delta t}{\Delta x} \left( C_{i+1} + C_{i-1} \right)
\]

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\[
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\]

\[
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\[
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\]

(1.25)
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Consider the explicit finite difference approximation of the 1-dimensional solute transport equation, where the advective term has been approximated by a central difference:

$$C_{i+1} = C_i - \frac{D}{2} \left( \frac{C_{i+1} - C_{i-1}}{2 \Delta x} \right)$$

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Consider the explicit finite difference approximation of the 1-dimensional solute transport equation, where the advective term has been approximated by a central difference:

$$\frac{C_{i+1} - C_i}{Dt} + \frac{C_{i+2} - C_{i-1}}{2Dt} = D \left( \frac{C_{i+1} - 2C_i + C_{i-1}}{Dx^2} \right)$$

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\[ u_{i+1} = u_i + \frac{1}{2} \left( \frac{a_{i+1} - a_i}{\Delta x} \right) (u_{i+1} - u_i) \]

\[ = u_i + \frac{1}{2} \left( \frac{a_{i+1} - a_i}{\Delta x} \right) u_{i+1} - \frac{1}{2} \left( \frac{a_{i+1} - a_i}{\Delta x} \right) u_i \]

\[ = \frac{1}{2} \left( \frac{a_{i+1} + a_i}{\Delta x} \right) u_{i+1} + \frac{1}{2} \left( \frac{a_{i+1} + a_i}{\Delta x} \right) u_i \]

\[ = \frac{1}{2} \left( \frac{a_{i+1} + a_i}{\Delta x} \right) (u_{i+1} + u_i) \]

\[ \text{Equation 125} \]
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\[ \frac{C_i^{n+1} - C_i^n}{\Delta t} + \frac{C_{i+1}^{n+1} - C_{i-1}^{n+1}}{2 \Delta x} = D \frac{C_{i+1}^{n} - 2C_i^{n} + C_{i-1}^{n}}{\Delta x^2} \]

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\[ C_{i+1}^n - C_{i}^n = \frac{D}{Dt} \left( C_{i+1}^n - C_{i}^n \right) \]

where \( C \) is the concentration, \( D \) is the dispersion coefficient, \( Dt \) is the time step, and \( x \) is the spatial coordinate.

\[ C_{i+1}^n = C_{i}^n + \frac{D}{Dt} \left( C_{i+1}^n - C_{i}^n \right) \]

This equation is the explicit finite difference approximation for the 1-dimensional solute transport equation.
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\[
C_{i+1}^n - C_i^n + D_{i+1}^n - D_i^n = D_{i+1}^n - D_i^n - D_{i+1}^n - D_i^n + D_{i+1}^n - D_i^n + D_{i+1}^n - D_i^n
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$$C_{i+1} + D_{i+1} - C_{i-1} - D_{i-1} = CV_{i} DT$$

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Solute Transport in Soil

http://dx.doi.org/10.5772/54557
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\[ \frac{C_i^n - C_i^{n-1}}{\Delta t} = \frac{C_{i+1}^n - C_{i-1}^n}{2\Delta x} \]

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Consider the explicit finite difference approximation of the 1-dimensional solute transport equation, where the advective term has been approximated by a central difference:

\[
\frac{S_{t+\Delta t} - S_{t}}{\Delta t} = \frac{D}{\Delta x^2} \left( S_{t}^{(1)} - 2S_{t} + S_{t}^{(2)} \right)
\]

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\[ C_{i+1} - C_{i-1} = \frac{D}{2} \frac{C_i}{\Delta t} \] 

(125)

Solute Transport in Soil

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79
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\[
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\]

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$$\frac{C_i^0 - C_i^0}{\Delta t} + \frac{\nu}{2\Delta x}(C_{i+1}^0 - C_{i-1}^0) - D\frac{2C_i^0 - C_{i+1}^0 - C_{i-1}^0}{(\Delta x)^2} = 0$$

(125)
Collecting terms, this can be rewritten as:

\[ C_i^n = \left( 1 - \frac{2D\Delta t}{(\Delta x)^2} \right) C_i^o + \left( \frac{\nu\Delta t}{2\Delta x} \right) C_{i-1}^o + \left( -\frac{\nu\Delta t}{2\Delta x} \right) C_{i+1}^o = \]

\[ (1 - \beta_1)C_i^o + \left( \beta_1 + \frac{\beta_2}{2} \right) C_{i-1}^o + \left( -\beta_1 + \frac{\beta_2}{2} \right) C_{i+1}^o \]

where:

\[ \beta_1 = \frac{\nu\Delta t}{2\Delta x}, \quad \beta_2 = \frac{2D\Delta t}{(\Delta x)^2} \]

Now assume that at a certain time a small error \( \epsilon \) (perturbation) is introduced in the solution to the equations. That can e.g. be caused by roundoff errors in a computer calculation. If we indicate the “correct” solution with \( C_\_ \), substitution of the perturbed solution \( C \) in the finite differenced equation (126) leads to:

\[ C_i^n + \epsilon_i^n = (1 - \beta_2)C_i^o + \left( \beta_1 + \frac{\beta_2}{2} \right) C_{i-1}^o + \left( -\beta_1 + \frac{\beta_2}{2} \right) C_{i+1}^o \]

\[ (1 - \beta_2)\epsilon_i^o + \left( \beta_1 + \frac{\beta_2}{2} \right) \epsilon_{i-1}^o + \left( -\beta_1 + \frac{\beta_2}{2} \right) \epsilon_{i+1}^o \]

Since the correct solution \( C \) obeys equation (126), we obtain the following equation for the perturbation \( \epsilon \):

\[ \epsilon_i^n = (1 - \beta_2)\epsilon_i^o + \left( \beta_1 + \frac{\beta_2}{2} \right) \epsilon_{i-1}^o + \left( -\beta_1 + \frac{\beta_2}{2} \right) \epsilon_{i+1}^o \]

The fact that the perturbation \( \epsilon \) is given by the same equation as the correct value of \( C \) is caused by the fact that the equation in \( C \) is a linear one.

Now consider one Fourier component of the perturbation given by:

\[ \epsilon_i = \lambda e^{i\omega x} \]
where $\omega$ is the wavenumber, and $\lambda$ the time dependent amplification factor. In order to have a stable solution, we will require that any perturbation $\epsilon$ in the solution will decrease with time for any wave number. Basically this means that $\lambda$ will decrease with time.

Substitution of (130) in (129) gives:

$$
\lambda^n e^{i\omega x} = (1 - \beta_2)\lambda^n e^{i\omega x} + \left(\beta_1 + \frac{\beta_2}{2}\right)\lambda^o e^{i\omega(x+\Delta x)} + \left(-\beta_1 + \frac{\beta_2}{2}\right)\lambda^o e^{i\omega(x+\Delta x)}
$$

(131)

Division by $\lambda^n e^{i\omega x}$ then gives:

$$
\frac{\lambda^n}{\lambda^o} = (1 - \beta_2) + \left(\beta_1 + \frac{\beta_2}{2}\right)e^{-i\omega\Delta x} + \left(-\beta_1 + \frac{\beta_2}{2}\right)e^{i\omega\Delta x} = 1 - \beta_2 - \beta_1 \left(e^{i\omega\Delta x} - e^{-i\omega\Delta x}\right) + \frac{\beta_2}{2} \left(e^{i\omega\Delta x} + e^{-i\omega\Delta x}\right)
$$

(132)

Now we will use the following relations:

$$
e^{i\omega\Delta x} - e^{-i\omega\Delta x} = 2i \sin(\omega\Delta x)
$$

$$
e^{i\omega\Delta x} + e^{-i\omega\Delta x} = 2 \cos(\omega\Delta x)
$$

(133)

Substitution in equation (132) then leads to:

$$
\frac{\lambda^n}{\lambda^o} = 1 - \beta_2 - 2\beta_1 i \sin(\omega\Delta x) + \beta_2 \cos(\omega\Delta x) = 1 - \beta_2 \left(1 - \cos(\omega\Delta x)\right) - 2\beta_1 i \sin(\omega\Delta x) = 1 - 2\beta_2 \sin^2\left(\frac{\omega\Delta x}{2}\right) - 2\beta_1 i \sin(\omega\Delta x)
$$

(134)

If we now take the absolute value, and substitute for shorthand $\theta=\omega\Delta x$, the following relation is obtained:

$$
\left|\frac{\lambda^n}{\lambda^o}\right| = \left(1 - 2\beta_2 \sin^2\frac{\theta}{2}\right)^2 + 4\beta_1^2 \sin^2\theta
$$

(135)

From well known goniometric relations:
Substitution in equation (135) gives, after rearranging terms:

\[
\frac{\lambda^n}{\lambda^o} = 1 - \left(4\beta_2 - 16\beta_1^2\right)\sin^2 \frac{\theta}{2} + \left(4\beta_2^2 - 16\beta_1^2\right)\sin^4 \frac{\theta}{2}
\]  

(137)

In order to have a stable solution, the absolute value of the ratio of \(\lambda^n/\lambda^o\) should be <1. Bearing in mind that both \(\sin^2\) and \(\sin^4\) are always positive, it is sufficient to require that:

\[
4\beta_2 - 16\beta_1^2 > 0  \quad 4\beta_2^2 - 16\beta_1^2 > 0
\]  

(138)

The second relation in (138) can be written as:

\[
\beta_2 < 1 \quad \text{or} \quad \Delta t < \frac{(\Delta x)^2}{2D}
\]  

(139)

and the first relation as:

\[
\beta_2 > 4\beta_1^2 \quad \text{or} \quad \Delta t < \frac{2D}{v^2}
\]  

(140)

Note, that in order to obtain a stable solution, both requirements (A-15) and (A-16) need to be fulfilled.

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