# Institut für Wasserbau · Universität Stuttgart



# Heft 87 Olaf Cirpka

CONTRACT: A Numerical Tool for Contaminant Transport and Chemical Transformations

## Heft 87

CONTRACT: A Numerical Tool for Contaminant Transport and Chemical Transformations – Theory and Program Documentation –

von Dipl.-Geoökol. Olaf Cirpka

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# Preface

Groundwater pollution control has become a growing challenge to water resources management. In this context groundwater research has to cope with the task of describing the processes influencing the input, spreading and chemical transformations of contaminants in aquifers in a quantitative manner, both as individual and as interactive processes.

In this context numerical simulation of groundwater flow, contaminant transport and chemical transformations is of primary importance because it provides the opportunity to integrate such different disciplines as hydromechanics, geology, chemistry and microbiology on a common quantitative basis. It also permits coupling of the results from field measurements to those from classical laboratory experiments for the prediction of field-scale reactive behaviour. Without numerical models the effects of single processes in complex interaction in reactive transport could hardly be distinguished. Therefore numerical simulation is an indispensable tool for present-day groundwater research.

As a prerequisite for the application of numerical methods, it must be ensured that the numerical tools used lead to a correct solution of the mathematical problem. Discretization errors leading to numerical diffusion or oscillatory behaviour may lead to erroneous results which may be misinterpreted as effects of chemical or physical processes. Requirements for the stability, the accuracy and the efficiency of the numerical methods are more strict and more difficult to fulfill for reactive transport than for conservative transport.

The present report written by Olaf Cirpka serves as an introduction to numerical methods for reactive multicomponent transport. Special emphasis is given to discretization methods for transport, and extensive comparisons of different approaches are presented. The given test cases for reactive transport indicate that conceptual models, such as the macrodispersion model or the two-domain approach, which are commonly used for conservative transport, may lead to incorrect results when applied to the transport of compounds which react with each other. However, the test cases also reveal the differences in qualitative behaviour between reactive transport and reactive systems in fully-mixed batch reactors.

This report includes the program documentation of the simulation tool *CONTRACT (Contaminant Transport and Chemical Transformations)* developed at the Institut für Wasserbau. For ease of communication with our international research partners, the report has been prepared in English.

Prof. Dr. h.c. Helmut Kobus, Ph.D.

# Vorwort

Der nachhaltige Schutz des Grundwassers vor anthropogenen Verunreinigungen gehört zu den drängenden Herausforderungen der Wasserwirtschaft. Vor diesem Hintergrund stellt sich der Grundwasserforschung die Aufgabe, die Prozesse, die den Eintrag, die Ausbreitung und die stofflichen Umwandlungen von Schadstoffen in Grundwasserleitern bestimmen, einzeln und in ihrer gegenseitigen Wechselwirkung quantitativ zu beschreiben.

Eine besondere Bedeutung kommt hierbei der numerischen Simulation der Grundwassertrömung, des Schadstofftransports und des Schadstoffabbaus zu. Sie ermöglicht es, unterschiedliche Fachdisziplinen wie die Strömungsmechanik, die Geologie, die Chemie und die Mikrobiologie auf einer gemeinsamen quantitativen Grundlage zu integrieren, sowie Ergebnisse aus dem Feld- und Labormaßstab miteinander zu verknüpfen. Wirkungen einzelner Prozesse in den gekoppelten Reaktions-Transport-Systemen ließen sich ohne Hilfe numerischer Modelle zumeist kaum quantifizieren.

Als Voraussetzung für den Einsatz von Simulationsmethoden muß zunächst sichergestellt sein, daß die eingesetzten numerischen Werkzeuge die mathematisch formulierten Probleme tatsächlich lösen und nicht durch Diskretisierungsfehler zu numerischer Diffusion oder zu Oszillationen und damit zu Ergebnisse führen, die ein qualitativ falsches physikalisches oder chemisches Verhalten vortäuschen. Hierbei stellt die Simulation reaktiver Transportvorgänge ungleich höhere Anforderungen an die Stabilität, Genauigkeit und Effizienz der numerischen Methoden als die Berechnung des konservativen Stofftransports.

Das vorliegende Mitteilungsheft von Herrn Dipl.-Geoökol. Olaf Cirpka gibt einen Einblick in die numerischen Methoden zur Simulation des reaktiven Multikomponenten-Transports. Ein besonderer Schwerpunkt wurde auf die Wahl der Diskretisierungsmethoden gelegt. Hierzu werden ausführliche Vergleichsrechungen vorgestellt. Die dargestellten Anwendungsbeispiele für den reaktiven Stofftransport verdeutlichen, daß Modellkonzepte wie der Makrodispersionsansatz oder das Doppelkontinuumsmodell, die sich für die Beschreibung des konservativen Stofftransports bewährt haben, nicht direkt auf den Transport von miteinander reagierenden Stoffen übertragen werden können. Sie zeigen jedoch auch, daß sich Reaktions-Transport-Systeme qualitativ von reinen Reaktions-Systemen in vollständig durchmischten Reaktoren unterscheiden.

Das Mitteilungsheft dient gleichzeitig als Programmbeschreibung für das am Institut für Wasserbau entwickelte Simulationsprogramm *CONTRACT (Contaminant Transport and Chemical Transformations)*. Im Hinblick auf die direkte Kooperation mit unseren internationalen Forschungspartnern wurde das Heft in englischer Sprache verfaßt.

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# **Chapter 1**

# **Problem Statement**

Contamination of the subsurface by organic compounds is a serious problem for the protection of groundwater. Although many organic pollutants have been shown to be degradable in laboratory studies most of them remain for years in the subsurface without reasonable attenuation. The availability of all necessary substrates such as electron acceptors, electron donors, primary carbon sources and in some cases cosubstrates or additional micronutrients has been identified as a limiting factor for biodegradation in aquifers.

*In-situ* bioremediation is based on injecting limiting substrates into the subsurface to stimulate microbial activity at the location of contamination. The delivery efficiency of compound injection is influenced firstly by advective-dispersive transport and hence by groundwater flow, secondly by mass transfer processes and finally by chemical transformations. This is shown schematically in Fig. 1.1.

A combination of chemical and microbial processes on the one hand and advective-dispersive transport on the other leads to a coupled problem, which may be expressed mathematically by coupled partial differential equations (PDE), ordinary differential equations (ODE) and algebraic equations (AE), all of which contain uncertainties.

Transport in groundwater is commonly described by the advection-dispersion equation derived in chapter 2. For this part of the problem 'only' the parameters are uncertain. In contrast to this the chemical part is uncertain on the conceptual level, where measures and processes of interest are defined in general. Equations to describe chemical transformations cannot always be proofed. And furthermore, parameter data for the equations are scarse.

Against this background a numerical tool to simulate the fate and behaviour of organic compounds in the subsurface should be flexible in the formulation of chemical processes so that it can be used for system identification. On the other hand it should be as accurate as possible for the calculation of known processes such as advective-dispersive transport, in order that differences between model calculations and measured data can clearly be interpreted as shortcoming in the identification or quantification of transformation processes. CONTRACT is a numerical model based on these requirements.



Figure 1.1: Processes of interest.

# Chapter 2

# **Governing Equations**

## 2.1 Continuity Equation

Calculation of transport requires the flow field to be known. This can be achieved by solving the continuity equation for groundwater flow, which can be derived from mass balance considerations for an infinitesimally small control volume in a porous medium. The following may be applied to calculate groundwater flow in a confined aquifer:

$$\nabla \cdot (\underline{v}_f) = q_{in,out} - S_0 \frac{\partial h}{\partial t}$$
(2.1.1)

Velocities in groundwater systems are typically in the range of less than 1m/day. For this case DARCY's linear law for calculating DARCY velocities  $v_f$  holds:

$$\underline{v}_f = \underline{k}_f \,\nabla h \tag{2.1.2}$$

Inserting (2.1.2) into (2.1.1) leads to:

$$S_0 \frac{\partial h}{\partial t} + \nabla \cdot (\underline{k}_f \nabla h) = q_{in,out}$$
(2.1.3)

The specific storage coefficient  $S_0$  is a characteristic measure for the storage capacity of a hydrogeological unit. For confined aquifers it is a function of the compressibility of both water and the rock matrix. Typical ranges are about  $5 \cdot 10^{-5}$  to  $5 \cdot 10^{-3}$ .

In unconfined aquifers the cross-section of flow is a function of the hydraulic head. Integrating over the depth from the bottom of an aquifer to the free groundwater surface thus leads to a non-linear form of the continuity equation:

$$hn_e \frac{\partial h}{\partial t} + \nabla \cdot (h\underline{\underline{k}}_f \nabla h) = Q_{in,out}$$
(2.1.4)

In this case the specific storage coefficient is replaced by the effective porosity which is about two orders of magnitude higher. Note that in the case of an unconfined aquifer, groundwater injection or extraction directly alters the volume of pores filled with water, whereas in the case of a confined aquifer this volume is almost constant and only compressibility contributes to the storage capacity.

## 2.2 Advective-Dispersive Transport

Balancing the mass of a dissolved compound in a infinitesimally small control volume of groundwater leads to the transport equation:

$$n_e \frac{\partial c}{\partial t} + \nabla \cdot (\underline{J}_m) - n_e r(c) = 0$$
(2.2.5)

where r(c) is the concentration change due to chemical transformations and mass transfer processes. Other mass inputs and outputs are neglected initially in this chapter.  $J_m$  is the mass flux of the dissolved compound and is defined for the advective-dispersive case by:

$$\underline{J}_m = n_e c \underline{v}_a - n_e \underline{\underline{D}} \,\nabla c \tag{2.2.6}$$

The seepage velocity  $\underline{v}_a$  describes the average time for advective transport of a compound between two points along a streamline. In contrast to this DARCY's velocity  $\underline{v}_f$  is the ratio of the discharge to the area of a cross-section perpendicular to the flow in the subsurface. The two velocities are proportional to each other, the proportionality factor being the effective porosity:

$$\underline{v}_a = \frac{1}{n_e} \underline{v}_f \tag{2.2.7}$$

The effective diffusion tensor  $\underline{D}$  includes molecular diffusion as well as of flow-related dispersion. For the one-dimensional case SCHEIDEGGER[53] defines the effective diffusion coefficient in the following way:

$$D = D_m + \alpha v_a \tag{2.2.8}$$

in which  $\alpha$  is the dispersivity. In the multidimensional case dispersion longitudinal to the flow direction greatly exceeds transverse dispersion. This may be accounted for by introducing dispersivities  $\alpha_l$  and  $\alpha_t$  for longitudinal and transverse dispersion, respectively. Provided the system of coordinates is along the direction of flow this leads to diagonal dispersion tensors:

$$\underline{\underline{D}} = \begin{bmatrix} D_l & 0 & 0\\ 0 & D_t & 0\\ 0 & 0 & D_t \end{bmatrix} \quad with \quad D_l = D_m + \alpha_l v_a$$

$$D_t = D_m + \alpha_t v_a$$
(2.2.9)

In the general case the tensor (2.2.9) has to be transformed into the general system of coordinates. For two-dimensional problems this leads to:

$$\underline{\underline{D}} = \begin{bmatrix} D_{xx} & D_{xy} \\ D_{yx} & D_{yy} \end{bmatrix} \quad with \quad D_{xx} = \alpha_l \frac{v_x^2}{v} + \alpha_t \frac{v_y^2}{v} + D_m$$

$$D_{xy} = D_{yx} = (\alpha_l - \alpha_t) \frac{v_x v_y}{v}$$

$$D_{yy} = \alpha_l \frac{v_y^2}{v} + \alpha_t \frac{v_x^2}{v} + D_m$$
(2.2.10)

and for three-dimensional problems:

$$\underline{\underline{D}} = \begin{bmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{bmatrix} \quad with \quad D_{xx} = \alpha_l \frac{v_x^2}{v} + \alpha_t \frac{v_y^2 + v_z^2}{v} + D_m$$

$$D_{xy} = D_{yx} = (\alpha_l - \alpha_t) \frac{v_x v_y}{v}$$

$$D_{xz} = D_{zx} = (\alpha_l - \alpha_t) \frac{v_x v_z}{v}$$

$$D_{yy} = \alpha_l \frac{v_y^2}{v} + \alpha_t \frac{v_x^2 + v_z^2}{v} + D_m$$

$$D_{yz} = D_{zy} = (\alpha_l - \alpha_t) \frac{v_y v_z}{v}$$

$$D_{zz} = \alpha_l \frac{v_z^2}{v} + \alpha_t \frac{v_x^2 + v_y^2}{v} + D_m$$

Inserting (2.2.6) and (2.2.7) into (2.2.5) and assuming constant porosities and fluid densities leads to:

$$n_e \frac{\partial c}{\partial t} + n_e \,\nabla \cdot (c\underline{v}_a) - n_e \,\nabla \cdot (\underline{\underline{D}} \,\nabla c) - n_e r(c) = 0 \tag{2.2.12}$$

Applying product the rule of differentiation to the advective mass flux term  $n_e \nabla \cdot (c\underline{v}_a)$  and introducing the continuity equation into the first resulting term leads to:

$$n_{e}\frac{\partial c}{\partial t} + c \nabla \cdot (\underline{v}_{f}) + n_{e}\underline{v}_{a} \cdot \nabla c - n_{e} \nabla \cdot (\underline{D} \nabla c) - n_{e}r(c) =$$

$$n_{e}\frac{\partial c}{\partial t} + c \left(q_{in,out} - S_{0}\frac{\partial h}{\partial t}\right) + n_{e}\underline{v}_{a} \cdot \nabla c - n_{e} \nabla \cdot (\underline{D} \nabla c) - n_{e}r(c) = 0$$
(2.2.13)

#### 2.2.1 Inflow and Outflow

Equation (2.2.13) was set up for a situation, in which no additional inputs of mass are taken into account. Hence mass fluxes across boundaries have to be added. These mass fluxes can be expressed by the product of discharge and concentration. At inflow boundaries the concentration in the incoming water  $c_{in}$  must be specified as a boundary condition, whereas at outflow boundaries the outflow concentration is the concentration resulting from the calculations. This means that the first term in the brackets of (2.2.13) vanishes. The resulting equation is:

$$n_e \frac{\partial c}{\partial t} + (c - c_{in})q_{in} - cS_0 \frac{\partial h}{\partial t} + n_e \underline{v}_a^T \nabla c - n_e \nabla \cdot (\underline{D} \nabla c) - n_e r(c) = 0$$
(2.2.14)

where  $q_{in}$  is the inflow discharge.

## 2.2.2 Depth-Integrated Transport Equation for Unconfined Aquifers

The transport equation (2.2.5) can be formulated in a depth-integrated manner for an unconfined aquifer by inserting (2.1.4) and (2.2.6) and including inflow and outflow boundary conditions:

$$n_e h \frac{\partial c}{\partial t} + (c - c_{in})Q_{in} - cn_e \frac{\partial h}{\partial t} + n_e h \underline{v}_a \cdot \nabla c$$

$$- n_e \nabla \cdot (h \underline{D} \nabla c) - n_e hr(c) = 0$$
(2.2.15)

#### 2.2.3 Two-Domain Approach

The main idea of the two-domain approach is to divide the pore volume of a porous medium into a mobile and an immobile fraction. Transport takes place only in the mobile fraction, and mass transfer between mobile and immobile porosity is expressed by a first order law [16]. This concept was originally developed to explain pore-scale effects such as "dead-end" pores or mass transfer between immobile soil aggregates and mobile macro-pores. However, the approach may be used to simplify large-scale heterogeneity [8].

The approach results in a system of two coupled equations for each compound, a partial differential equation for the concentration in the mobile domain and an ordinary differential equation for the concentration in the immobile domain:

$$n_{mob}R_{i}\frac{\partial c_{i}^{mob}}{\partial t} + \nabla \cdot \left(\underline{v}_{a}c_{i}^{mob} - n_{mob}\underline{\underline{D}}\nabla c_{i}^{mob}\right) - n_{mob}r_{i}^{mob} + k_{m\leftrightarrow i}(c_{i}^{imm} - c_{i}^{mob}) = 0$$

$$(2.2.16)$$

$$n_{imm}R_i\frac{\partial c_i^{imm}}{\partial t} - n_{imm}r_i^{imm} - k_{m\leftrightarrow i}(c_i^{imm} - c_i^{mob}) = 0$$
(2.2.17)

in which subscripts *mob* and *imm* refer to the mobile and immobile porosity, respectively, and  $k_{m\leftrightarrow i}$  is the first-order mass transfer coefficient. Note that the seepage velocity  $\vec{v}_e$  for the evaluation of  $\underline{D}$  in (2.2.16) must be related to the mobile porosity rather than to total porosity.

## 2.3 Sorption

#### 2.3.1 Local Equilibrium Assumption

Mass transfer between a dissolved phase and a sorbing surface is by nature a kinetic process. Nevertheless, the characteristic time of mass transfer may be reasonably smaller than the characteristic time of advective-dispersive transport, i.e. local equilibrium can be assumed without introducing a significant error. Equilibrium may be expressed by sorption 'isotherms', plots showing the equilibrium concentration in the sorbed phase as a function of the concentration in the dissolved phase. These isotherms are measured in batch experiments and can be interpretated on the basis of theoretical considerations.

#### 2.3.1.1 Linear Partitioning

Linear partitioning is the simpliest concept for describing sorption. The ratio between the sorbed and dissolved concentration is assumed to be constant. For reasons of simplification the sorbed concentration may be related here to the pore volume and not, as conventionally defined, to the matrix volume:

$$c_{sorb}^* = K_d c_w \tag{2.3.18}$$

The partitioning coefficient  $K_d$  includes the ratio of the matrix volume to the pore volume and the sorptivity of the substance at the surfaces. A common model for hydrophobic organic substances is to assume that sorption takes place only at the natural organic matter of the soil. This assumption leads to the  $f_{OC}K_{OC}$  model in which the partitioning coefficient can be calculated from the porosity  $n_e$ , the organic carbon content  $f_{OC}$  and a partitioning coefficient  $K_{OC}$  between organic carbon and water, which is assumed to be a substance-specific constant:

$$K_d = \frac{1 - n_e}{n_e} f_{oc} K_{oc}$$
(2.3.19)

#### 2.3.1.2 Nonlinear Sorption Isotherms

The concept of linear partitioning assumes that the distribution of a compound between sorbed and dissolved phases is not influenced by the concentration. This might be true for low concentrations where sorption is influenced only by interactions between almost free surfaces and dissolved compounds of interest. At higher concentrations an interaction between the dissolved compounds and the

compounds already sorbed at the surface must also be considered. Two kinds of interaction with contrary effects are possible: If there is only a certain number of sorbing sites at the surface, increasing the dissolved concentration would lead to a decreasing ratio of sorbed compounds as there are less sorption sites available. On the other hand, sorbed compounds themselves could act as sorbing sites for dissolved compounds. This would lead to an increase in the partitioning coefficient with increasing concentrations. The first case is stated much more in the literture than the latter, even though both kinds of interaction occur.

The concept of LANGMUIR is based on the assumption that a certain maximum sorption capacity can be defined. This maximum capacity is approached asymptotically by increasing the concentration in the dissolved phase:



The concept of FREUNDLICH does not include such a maximum sorption capacity. Nevertheless, sorptivity of the surface is decreasing with increasing concentrations:

$$c_{sorb}^* = K c_w^{1/n}$$

$$log(c_{sorb}^*) = logK + \frac{1}{n} logc_w$$
(2.3.21)

The paramters K and n in (2.3.21) can be derived by applying linear regression to the sorption isotherm represented in a double-logarithmic plot of measured data.

#### 2.3.2 Incorporating Sorption into the Transport Equation

Under the assumption of local equilibrium mass transfer can easily be introduced into the transport equation (2.2.14):

$$n_{e}\frac{\partial c_{w}}{\partial t} + n_{e}\frac{\partial c_{sorb}^{*}}{\partial t} + (c_{w} - c_{in})q_{in} - c_{w}S_{0}\frac{\partial h}{\partial t} + n_{e}\underline{v}_{a} \cdot \nabla c \qquad (2.3.22)$$
$$- n_{e}\nabla \cdot (\underline{D}\nabla c_{w}) - n_{e}r(c_{w}) = 0$$

In (2.3.22) it is assumed that transport and chemical interactions only take place in the dissolved phase. Sorbed mass is only considered to act as a storage term. The term  $\partial c_{sorb}^* / \partial t$  can be transformed into:

$$\frac{\partial c_{sorb}^*}{\partial t} = \frac{\partial c_s}{\partial c_w} \frac{\partial c_w}{\partial t}$$
(2.3.23)

and hence (2.3.22) can be transformed into:

$$Rn_{e}\frac{\partial c}{\partial t} + (c - c_{in})q_{in} - cS_{0}\frac{\partial h}{\partial t} + n_{e}\underline{v}_{a} \cdot \nabla c$$

$$- n_{e}\nabla \cdot (\underline{D}\nabla c) - n_{e}r(c) = 0$$

$$(2.3.24)$$

in which R is the retardation factor defined by:

$$R = 1 + \frac{\partial c_{sorb}^*}{\partial c_w} \tag{2.3.25}$$

Dividing (2.3.24) by the retardation factor shows that retardation slows down transport processes (for this *retardation*). In the case of a linear sorption isotherm R is independent of concentration. In the case of a LANGMUIR or FREUNDLICH isotherme R decreases with increasing concentration. This leads to tailing of a peak. In contrast to this a concave sorption isotherm would lead to fronting effects.

#### 2.3.3 Sorption Kinetics

Adsorption, absorption and desorption processes are related to mass transfer across boundary layers at least in the dissolved phase and in some cases in the sorbed phase as well (organic coating, porous cores, etc.). On the molecular scale this mass transfer is a diffusive process. Thus mass transfer is limited by the diffusion coefficient, by the thickness of the diffusive layer and in some cases by advective processes in non-diffusive boundary layers. Depending on boundary layer thickness, equilibrium conditions, diffusion coefficients and flow velocity, mass transfer must be treated as slow or fast process, whereby a slow process is expressed by an ordinary differential equation (ODE) and a fast process leads to the local equilibrium assumption. The simpliest model for kinetic-controlled mass transfer is

the first order kinetics approach in which the mass flux is proportional to the difference between the equilibrium and actual concentration:

$$\frac{\partial c_w}{\partial t} = \alpha_{sorb} \left( \frac{c_{sorb}^*}{K_d} - c_w \right) \tag{2.3.26}$$

First order kinetics only approximately descirbes kinetic-controlled mass transfer, as the entire sorbed mass is assumed to be involved in mass transfer. More sophisticated models also take into account the penetration of sorbing cores. In these models diffusion processes are calculated directly. This leads to mass transfer coefficients dependent on sorption history.

## 2.4 Microbial Growth and Related Chemical Transformations

#### 2.4.1 Conceptual Model

Stimulation of microbial activity requires fulfillment of at least the following criteria:

- The presence of microbes catalyzing the biotransformations of interest,
- Availability of an appropriate electron acceptor and an appropriate electron donor,
- Availability of a primary carbon source for microbial growth,
- Sufficiently high concentrations of additional nutrients,
- Absence of toxic factors.

Provided these conditions are fulfilled, microbial biomass should grow and consume electron acceptors, electron donors and primary carbon sources. The contaminant can be the electron acceptor in a reductive degradation pathway, the electron donor in an oxidative degradation pathway or neither of them in the case of cometabolism. In the latter case microbiota produce enzymes catalyzing a reaction which destroys the contaminant, while contaminant destruction itself does not stimulate microbial growth.

#### 2.4.2 Substrate Consumption

#### 2.4.2.1 Michaelis-Menten Kinetics

Although MICHAELIS-MENTEN kinetics was originally developed for enzyme kinetics it has often been applied to model more complex systems. The concept is based on the assumption that a certain concentration of enzymes is present. The reaction consists of two reaction steps: the attachment of the aqueous compound to the reactive site of the enzyme and the release of the transformed compound from the enzyme:

$$A + E_f \xrightarrow{r_1} AE \xrightarrow{r_2} A^* + E_f \tag{2.4.27}$$

in which A is the original aqueous compound,  $A^*$  is the transformed compound,  $E_f$  is the free enzyme and AE is the complex of the enzyme with A. Under steady-state conditions the reaction rate for the first step  $r_1$  equals the reaction rate for the second step  $r_2$ . The reaction rate  $r_1$  is assumed to be proportional to  $A \cdot E_f$ , and the rate  $r_2$  is assumed to be proportional to AE. Introducing the total concentration of enzymes  $E_t$  then yields:

$$r_{1} = k_{1} A \cdot E_{f}$$

$$r_{2} = k_{2} AE$$

$$r_{2} = r_{1} = r$$

$$E_{f} = E_{t} - AE$$

$$\Rightarrow k_{1} A (E_{t} - AE) = k_{2} AE$$

$$\Rightarrow AE = \frac{A}{\frac{k_{2}}{k_{1}} + A} E_{t}$$

$$\Rightarrow r = \tilde{r}_{max} \frac{A}{K_{m}^{A} + A} \cdot E_{t}$$
(2.4.28)

in which  $\tilde{r}_{max} = k_2$  is the maximum reaction rate per unit enzyme and  $K_m^A = k_2/k_1$  is the MICHAELIS-MENTEN or MONOD coefficient. The dependency of reaction rates on concentration is linear for low concentrations as enzymes are not limiting. At high concentrations reaction rates do not increase with increasing concentrations as all enzymes are already activated. The MICHAELIS-MENTEN terms are similiar to LANGMUIR isotherm (2.3.21) for sorption.

Assuming that the concentration of enzymes is proportional to the biomass concentration and that the coupled transformation of several reacting compounds (e.g. electron acceptor and electron donor) can be described by the products of single MICHAELIS-MENTEN terms leads to:

$$r_j = \tilde{r}_{max}^j X \prod_{i=1}^{n_{Sub}} \frac{c_i}{K_m^i + c_i}$$
(2.4.29)

in which  $\tilde{r}_{max}^{j}$  is the maximum reaction rate of compound j related to the biomass concentration X,  $n_{Sub}$  is the number of substances interacting,  $r_{j}$  converges to  $\tilde{r}_{max}^{j}X$  at high concentrations, and a linear relationship with a slope of  $\tilde{r}_{max}^{j}X/K_{m}^{i}$  is attained at low concentrations.

#### 2.4.3 Inhibitory Effects

#### 2.4.3.1 Substrate Inhibition

In some cases one of the substrates degraded by the microbiota becomes toxic at higher concentrations. One possibility of accounting for this is to apply HALDANE's extended version of the MICHAELIS-MENTEN equation:

$$r_{j} = \tilde{r}_{max}^{j} X \prod_{i=1}^{n_{Sub}} \frac{c_{i}}{K_{m}^{i} + c_{i} + \frac{c_{i}^{2}}{K_{i}^{i}}}$$
(2.4.30)

in which  $K_i^i$  is the inhibition concentration and  $r_j$  converges to zero when  $c_i$  becomes much larger than  $K_i^i$ .

#### 2.4.3.2 Inhibition by other Compounds

Inhibition by other compounds can be expressed by additional factors which are equal to unity for  $c_{inh} = 0$  and converge to zero at high concentrations. One possible expression is as follows:

$$r_j = \dots \cdot \frac{K_{inh}^i}{K_{inh}^i + c_{inh}}$$
(2.4.31)

#### 2.4.3.3 Competitive Inhibition

Considering two competing reactions of two aqueous compounds A and B with the same reactive site of an enzyme E yields:

$$\begin{array}{cccc} A + E_f & \stackrel{r_1}{\to} & AE & \stackrel{r_2}{\to} & A^* + E_f \\ B + E_f & \stackrel{r_3}{\to} & BE & \stackrel{r_4}{\to} & B^* + E_f \end{array}$$
(2.4.32)

 $A^*$  and  $B^*$  are now the transformed compounds,  $E_f$  is the free enzyme, and AE and BE are the complexes of the enzyme with A and B, respectively. The concentration of the free enzymes is now

dependent on both complexes:

$$r_{1} = k_{1} A \cdot E_{f}$$

$$r_{2} = k_{2} AE$$

$$r_{3} = k_{3} B \cdot E_{f}$$

$$r_{4} = k_{4} BE$$

$$E_{f} = E_{t} - AE - BE$$

$$k_{1} A (E_{t} - AE - BE) = k_{2} AE$$

$$k_{3} B (E_{t} - AE - BE) = k_{4} BE$$

$$AE = \frac{A}{K_{m}^{A} + A} (E_{t} - BE)$$

$$BE = \frac{B}{K_{m}^{B} + B} (E_{t} - AE)$$

$$(2.4.33)$$

in which  $K_m^A = k_2/k_1$  and  $K_m^B = k_4/k_3$ . The following is obtained after rearrangements:

$$AE = \frac{A}{K_m^A \left(1 + \frac{B}{K_m^B}\right) + A} E_t$$
  

$$BE = \frac{B}{K_m^B \left(1 + \frac{A}{K_m^A}\right) + B} E_t$$
  

$$\Rightarrow r_A = \tilde{r}_{max}^A \frac{A}{K_m^A \left(1 + \frac{B}{K_m^B}\right) + A} E_t$$
  

$$\Rightarrow r_B = \tilde{r}_{max}^B \frac{B}{K_m^B \left(1 + \frac{A}{K_m^A}\right) + B} E_t$$
  
(2.4.34)

(2.4.34) may be interpreted as a decrease in the apparent  $K_m^i$  value if several compounds compete at the same reaction site. Assuming again that the concentration of enzymes is proportional to the biomass concentration and that multiplication of several modified MICHAELIS-MENTEN terms expresses the dependency on several interacting compounds leads to (2.4.35):

$$r_j = \tilde{r}_{max}^j X \prod_{i=1}^{n_{Sub}} \frac{c_i}{K_m^i \left(1 + \sum \frac{c_k}{K_m^k}\right) + c_i}$$
(2.4.35)

in which the subscript k describes all compounds competing with compound i at the reaction site.

#### 2.4.4 Microbial Growth

In the case where the primary carbon source coincides with the electron donor, microbial growth is proportional to consumption rates. Assuming MICHAELIS-MENTEN dependency for both electron

acceptor and donor leads to the following coupled system of equations:

$$k_{gr} = \mu_{max} \frac{c_D}{K_D + c_D} \frac{c_A}{K_A + c_A}$$

$$\frac{\partial X}{\partial t} = (k_{gr} - k_{dec}) X$$

$$\frac{\partial c_D}{\partial t} = \frac{k_{gr} X}{Y_D}$$

$$\frac{\partial c_A}{\partial t} = \frac{k_{gr} X}{Y_A}$$

$$(2.4.36)$$

in which  $\mu_{max}$  is the maximum growth rate,  $k_{gr}$  is the actual growth rate and  $k_{dec}$  is a first-order decay rate for biomass. The subscripts D and A denote the electron donor and acceptor, respectively.

If the primary carbon source does not coincide with the electron donor or acceptor, microbial growth and degradation rates are coupled in such a way, that degradation rates are independent of the primary carbon source concentration whereas microbial growth is dependent on the latter:

$$k_{gr} = \tilde{\mu}_{max} \frac{c_D}{K_D + c_D} \frac{c_A}{K_A + c_A}$$

$$\frac{\partial X}{\partial t} = \left( k_r \frac{c_P}{K_P + c_P} - k_{dec} \right) X$$

$$\frac{\partial c_D}{\partial t} = \frac{k_r X}{Y_D}$$

$$\frac{\partial c_A}{\partial t} = \frac{k_r X}{Y_A}$$

$$\frac{\partial c_P}{\partial t} = \frac{c_P}{K_P + c_P} \frac{k_r X}{Y_P}$$

$$(2.4.37)$$

In addition to the first set of equations, in (2.4.37) the primary carbon source (denoted by P) also occurs.  $k_r$  is the reaction rate.

# **Chapter 3**

# **Transport Calculation**

Several approaches are possible for solving the transport equation. They may be subdivided into LANGRANGIAN, EULERIAN-LANGRANGIAN and EULERIAN methods.

- LANGRANGIAN methods are based on the characteristic form of the transport equation. In the classical particle tracking/ random walk method, particles carrying masses are tracked through the aquifer. These methods are not considered in this paper.
- EULERIAN-LANGRANGIAN methods split the transport equation into the hyperbolic part, which is solved by LANGRANGIAN methods, and the parabolic part which is solved by EULERIAN methods. Alternatively to that a space-time EULERIAN method may be applied, in which the boundaries of the control volumes follow characteristics in the space-time domain. See (3.3.114).
- In EULERIAN methods fixed control volumes are observed. Eulerian approaches are therefore the most direct means of solving the partial differential equations. Unfortunately, however, stability problems may occur if the solution is discontinuous and if advective transport exceeds diffusion.

The choice of method for the calculation of transport is dependent on the requirements of chemical calculations and coupling:

- Chemical calculations require concentrations in definite spatial units. Masses on particles would first have to be converted into concentrations in domains, thus destroying the accuracy of the particle tracker algorithm.
- Different compounds may follow different characteristics. This leads to complications in EU-LERIAN-LANGRANGIAN methods if an implicit coupling method is chosen.
- Chemical transformations can be treated as reactive sink/source terms in the transport calculation. If such a coupling approach is chosen the transport algorithm must be capable of dealing with multiple sink/source terms independent of the flow field.
- Transformation rates are very sensitive to mixing of compounds. Hence artificial diffusion in the transport calculation must be minimized.

• The equations describing chemical transformations are instable in the negative concentration range. As a consequence monotonicity of the transport algorithm is required.

The last two points reflect typical problems associated with EULERIAN approaches, the first three points reflect problems which arise using (partially) LANGRANGIAN methods.

In CONTRACT only EULERIAN approaches are applied. CONTRACT-FE is based on the Finite Element Method (FEM), whereas CONTRACT-2 and CONTRACT-3 are based on the integrated Finite Difference Method (FDM). Principles of the methods are explained in the following sections.

## **3.1** Criteria for the Quality of Numerical Methods

Only for specific initial and boundary conditions the exact solution of the transport equation may be derived by analytical methods. Therefore numerical methods are used. In numerical methods the model problem is discretized in space and time, thus providing a solution at discrete nodes only. For any point between the nodes interpolation is necessary. The method of interpolation is dependent on the chosen method of discretization (e.g. linear interpolation, piecewise constant approximation, etc.).

The application of discretization techniques such as FEM or FDM generally leads to numerical errors which are dependent on the discretization in space and time. Exact nodal values can only be achieved in special test cases.

#### 3.1.1 Accuracy

The most common method used to quantify discretization errors is truncation error analysis. Truncation error analysis is based on the TAYLOR evolution of nodal values. A rectangular grid and constant coefficients must be applied. In the case of FEM the system of element equations must be transformed into an equation for one particular nodal value as a function of the values at the surrounding nodes in space and time (stencil). Finally, the nodal values at the surrounding nodes are replaced by TAYLOR evolution series of the value of interest. The resulting partial differential equation is compared with the original partial differential equation to be solved. The remaining terms form the truncation error. The order of consistency designates the order of the lowest derivative of the truncation error. For instance, second order errors in space are diffusive errors.

As TAYLOR evolution is only applicable for continuously differentiable functions the truncation error gives no indication as to whether a scheme yields reasonable results in the proximity of discontinuities. However, for smooth solutions the truncation error is a correct measure of accuracy. Truncation error analysis indicates in any particular case whether a scheme converges to the correct solution when the discretization is refined.

## 3.1.2 Stability

Stability describes how sensitive a numerical scheme reacts to errors introduced into the approximate solution. A scheme amplifying small errors is unstable as even higher order truncation errors can lead to significant oscillations. A scheme which damps errors is stable as higher order truncation errors are cancelled out. Unfortunately, the fact that linear stable schemes have an order of consistency of not more than unity means that they lead to artificial diffusion.

Monotonicity or monotonic convergence is a property which includes stability. Monotonic convergence implies that:

- Refinement of discretization reduces the dicretization error (convergence) and
- the local sign of the error does not change (monotonic behaviour).

Fig. 3.1 illustrates that alternating convergence leads to oscillations whereas no oscillations occur in the case of monotonic convergence.

## 3.2 Integrated Finite Difference Method

#### 3.2.1 General Approach

The Finite Difference Method (FDM) is the simpliest approach in terms of spatial discretization: the domain is simply divided into rectangular cells. In the integrated FDM approach the integrated form of the transport equation (2.2.5) is solved:

$$\int_{V} n_e \frac{\partial c}{\partial t} dV + \int_{\Gamma} \underline{n} \cdot \underline{J}_m d\Gamma - \int_{V} n_e r(c) dV = 0$$
(3.2.1)

in which V is the volume of a cell and  $\Gamma$  its boundary. For a regular 2-D cell the integrals are solved easily:

$$\left(\frac{\partial c_{i,j}}{\partial t} - r\right) n_e \Delta x_i \Delta y_j \Delta z_{i,j} + \left(J_{i+1/2,j}^x - J_{i-1/2,j}^x\right) \Delta y_j \Delta z_{i,j} + \left(J_{i,j+1/2}^y - J_{i,j-1/2}^y\right) \Delta x_i \Delta z_{i,j} = 0$$
(3.2.2)

in which *i* and *j* are cell subscripts for the x and y direction, respectively, and  $J_{i+1/2,j}^x$  is the mass flux in the x direction at the boundary between cell *i*, *j* and *i* + 1, *j*. This implies a one-point integration of mass fluxes.



**Alternating Convergence** 



Figure 3.1: Monotonic and alternating convergence.

## 3.2.2 Evaluation of Velocities

For the calculation of mass fluxes, seepage velocities must first be evaluated. Velocities at intercell boundaries have boundary designators (e.g.  $v_x(i + 1/2, j)$ ). Velocities at cell centers have cell designators (e.g.  $v_x(i, j)$ ). For a two-dimensional domain these velocities can be calculated from:

$$v_x(i,j) = -\frac{k_f^{xx}(i,j)}{n_e(i,j)} \frac{\partial h}{\partial x}(i,j) - \frac{k_f^{xy}(i,j)}{n_e(i,j)} \frac{\partial h}{\partial y}(i,j)$$

$$v_y(i,j) = -\frac{k_f^{yy}(i,j)}{n_e(i,j)} \frac{\partial h}{\partial y}(i,j) - \frac{k_f^{xy}(i,j)}{n_e(i,j)} \frac{\partial h}{\partial x}(i,j)$$
(3.2.3)

(3.2.3) holds for the evaluation of velocities at intercell boundaries as well as for velocities at cell centers. In the first case the hydraulic conductivity and the porosity must be evaluated from the harmonic mean of the cell values:

$$n_{e}(i+1/2,j) = \frac{2n_{e}(i,j)n_{e}(i+1,j)}{n_{e}(i,j) + n_{e}(i+1,j)}$$

$$k_{f}^{xx}(i+1/2,j) = \frac{2k_{f}^{xx}(i,j)k_{f}^{xx}(i+1,j)}{k_{f}^{xx}(i,j) + k_{f}^{xx}(i+1,j)}$$

$$k_{f}^{xy}(i+1/2,j) = \frac{2k_{f}^{xy}(i,j)k_{f}^{xy}(i+1,j)}{k_{f}^{xy}(i,j) + k_{f}^{xy}(i+1,j)}$$

$$k_{f}^{yy}(i+1/2,j) = \frac{2k_{f}^{yy}(i,j)k_{f}^{yy}(i+1,j)}{k_{f}^{xx}(i,j) + k_{f}^{yy}(i+1,j)}$$
(3.2.4)

The gradients can be approximated by simple linear interpolation:

$$\begin{aligned} \frac{\partial h}{\partial x}(i,j) &= 2\frac{h(i+1,j) - h(i-1,j)}{\Delta x(i+1) + 2\Delta x(i) + \Delta x(i-1)} \\ \frac{\partial h}{\partial y}(i,j) &= 2\frac{h(i,j+1) - h(i,j-1)}{\Delta y(j+1) + 2\Delta y(j) + \Delta y(j-1)} \\ \frac{\partial h}{\partial x}(i+1/2,j) &= 2\frac{h(i+1,j) - h(i,j)}{\Delta x(i+1) + \Delta x(i)} \\ \frac{\partial h}{\partial y}(i+1/2,j) &= \frac{h(i,j+1) + h(i+1,j+1) - h(i,j-1) + h(i+1,j-1)}{\Delta y(j+1) + 2\Delta y(j) + \Delta y(j-1)} \\ \frac{\partial h}{\partial y}(i,j+1/2) &= 2\frac{h(i,j+1) - h(i,j)}{\Delta y(j+1) + \Delta y(j)} \\ \frac{\partial h}{\partial x}(i,j+1/2) &= \frac{h(i+1,j) + h(i+1,j+1) - h(i-1,j) + h(i-1,j+1)}{\Delta x(i+1) + 2\Delta x(i) + \Delta x(i-1)} \end{aligned}$$
(3.2.5)

For boundary nodes evaluation of some of the gradients are not definite as no cells beyond the boundary exist. One possible solution to this is to set subscripts beyond the boundary to boundary subscripts.

#### 3.2.3 Diffusive Mass Fluxes

Calculation of diffusive mass fluxes is equivalent to the calculation of velocities (3.2.3):

$$J_{i+1/2,j}^{x,diff} = -n_e(i+1/2,j) \quad \left( D^{xx}(i+1/2,j) \frac{\partial c}{\partial x}(i+1/2,j) \right)$$
(3.2.6)

$$+D^{xy}(i+1/2,j)\frac{\partial c}{\partial y}(i+1/2,j)\left)$$

$$J^{y,diff}_{i,j+1/2} = -n_e(i,j+1/2) \left(D^{yy}(i,j+1/2)\frac{\partial c}{\partial y}(i,j+1/2) + D^{yx}(i,j+1/2)\frac{\partial c}{\partial x}(i,j+1/2)\right)$$
(3.2.7)

Note that the definition of the dispersion tensor (2.2.10) requires velocities at intercell boundaries normal to the intercell boundary, which is defined above, and also parallel to it. For the latter innercell velocities should be calculated and averaged by taking the harmonic mean. Longitudinal and transverse dispersivity may also be averaged by taking the harmonic means:

$$v_{x}(i, j + 1/2) = \frac{2v_{x}(i, j)v_{x}(i, j + 1)}{v_{x}(i, j) + v_{x}(i, j + 1)}$$

$$\alpha_{l}(i, j + 1/2) = \frac{2\alpha_{l}(i, j)\alpha_{l}(i, j + 1)}{\alpha_{l}(i, j) + \alpha_{l}(i, j + 1)}$$

$$\alpha_{t}(i, j + 1/2) = \frac{2\alpha_{t}(i, j)\alpha_{t}(i, j + 1)}{\alpha_{t}(i, j) + \alpha_{t}(i, j + 1)}$$
(3.2.8)

Concentration gradients are equivalent to head gradients in (3.2.5):

$$\frac{\partial c}{\partial x}(i+1/2,j) = 2\frac{c(i+1,j) - c(i,j)}{\Delta x(i+1) + \Delta x(i)}$$

$$\frac{\partial c}{\partial y}(i+1/2,j) = \frac{c(i,j+1) + c(i+1,j+1) - c(i,j-1) + c(i+1,j-1)}{\Delta y(j+1) + 2\Delta y(j) + \Delta y(j-1)}$$

$$\frac{\partial c}{\partial y}(i,j+1/2) = 2\frac{c(i,j+1) - c(i,j)}{\Delta y(j+1) + \Delta y(j)}$$

$$\frac{\partial c}{\partial x}(i,j+1/2) = \frac{c(i+1,j) + c(i+1,j+1) - c(i-1,j) + c(i-1,j+1)}{\Delta x(i+1) + 2\Delta x(i) + \Delta x(i-1)}$$
(3.2.9)

Note that cross-diffusion terms can lead to oscillations when discontinuities occur (namely under heterogeneous conditions). Ignoring cross-diffusion terms is thus leading to monotonic but inaccurate solutions. This property is important for the implementation of the flux-corrected transport (FCT) algorithm (see section 3.2.4.2.1).

#### 3.2.4 Advective Mass Fluxes

Calculation of advective mass fluxes is again equivalent to the calculation of diffusive mass fluxes (3.2.6) and velocities (3.2.3). The main difference is that in advective transport the concentration

itself is involved rather than its spatial derivative:

$$J_{i+1/2,j}^{x,adv} = n_e(i+1/2,j)v_x(i+1/2,j)c(i+1/2,j)$$
(3.2.10)

$$J_{i,j+1/2}^{y,adv} = n_e(i,j+1/2)v_y(i,j+1/2)c(i,j+1/2)$$
(3.2.11)

The main problem of (3.2.10) is how to determine the concentrations at the intercell boundaries c(i + 1/2, j) and c(i, j + 1/2). In the following sections two linear schemes and two non-linear schemes are presented.

#### 3.2.4.1 Linear Differentiation Schemes

So-called upwinding is a common method appled in FDM to stabilise the solutions of hyperbolic partial differential equations. Since the flux of information for pure advective transport is only in the direction of flow, the advective mass flux at an edge is defined by the product of the velocity normal to the edge, the interface cross-section and the concentration in the upstream (or 'upwind') cell. In contrast to this, the average concentrations in the donor and acceptor cells are used for calculating the advective mass flux when applying central differentiation.

$$c^{cd}(i+1/2,j) = \frac{c(i,j) + c(i+1,j)}{2}$$
(3.2.12)

$$c^{up}(i+1/2,j) = \begin{cases} c(i,j) & \text{if } v_x(i+1/2,j) > 0\\ c(i+1,j) & \text{if } v_x(i+1/2,j) < 0 \end{cases}$$
(3.2.13)

Any mixing of upwind and central differentiation is possible by means of an interpolation coefficient  $\alpha$  ranging from 0 to 1:

$$c^{\alpha}(i+1/2,j) = \alpha c^{up}(i+1/2,j) + (1-\alpha)c^{cd}(i+1/2,j)$$
(3.2.14)

The principles of upwind and central differentiation are shown in Fig. 3.2.

Notice that upwind differentiation leads to exact nodal values for advective transport if the COURANT number equals unity. However, for COURANT numbers different from unity upwind differentiation introduces artificial diffusion. Applying upwind differentiation leads to a monotonic scheme. In contrast to the latter central differentiation is of second order accuracy, thus non-diffusive. However, central differentiation is not monotonic.

#### 3.2.4.2 Higher Order Monotonic Schemes

**3.2.4.2.1** Flux Corrected Transport Flux-Corrected Transport is a method developed by BORIS & BROOKS [3] and ZALESAK [72]. The basic idea is to combine a low order monotonic method and



Approximation of Advective Mass Flux over Cell Edges

v Defined at Cell Edges (see above) Approximation of c by Averaging or Choice of Upstream Concentration



Figure 3.2: Upwind and central differentiation in FDM.

a high order method. A time step has to be solved for both methods. Higher order fluxes are then limited in such a way that no new extrema with respect to the low order solution and the old time step occur. Hence monotonicity of the low order solution is preserved. The principle of the method is explained in Fig. 3.3.

Mass fluxes F for the low and high order scheme first must be evaluated independently. The subscripts h and l indicate the high order and low order scheme, respectively. After solving the time step by both methods an antidiffusive flux  $F_{ad}$  can be calculated:

$$F_{h}^{x}(i+1/2,j) = J_{h}^{x}(i+1/2,j)\Delta y_{j}\Delta z_{i,j}$$

$$F_{l}^{x}(i+1/2,j) = J_{l}^{x}(i+1/2,j)\Delta y_{j}\Delta z_{i,j}$$

$$F_{h}^{y}(i,j+1/2) = J_{h}^{y}(i,j+1/2)\Delta x_{j}\Delta z_{i,j}$$

$$F_{l}^{y}(i,j+1/2) = J_{l}^{y}(i,j+1/2)\Delta x_{j}\Delta z_{i,j}$$

$$F_{ad}^{x}(i+1/2,j) = F_{h}^{x}(i+1/2,j) - F_{l}^{x}(i+1/2,j)$$
(3.2.15)



Figure 3.3: Principle of the Flux-Corrected Transport Method.

$$F_{ad}^{y}(i, j+1/2) = F_{h}^{y}(i, j+1/2) - F_{l}^{y}(i, j+1/2)$$

These antidiffusive fluxes must be limited to preserve monotonicity by a factor  $T_{i+1/2,j}$  or  $T_{i,j+1/2}$ , respectively, specific to the intercell boundary of interest:

$$F_{ad}^{x,c}(i+1/2,j) = T_{i+1/2,j}F_{ad}^{x}(i+1/2,j)$$

$$F_{ad}^{y,c}(i,j+1/2) = T_{i,j+1/2}F_{ad}^{y}(i,j+1/2)$$
(3.2.16)

in which  $T_{i+1/2,j}$  and  $T_{i,j+1/2}$  can vary from 0 to 1. Summarizing all corrected antidiffusive fluxes related to a cell leads to the correction of the low order solution:

$$\Delta c^{i,j} = F_{ad}^{x,c}(i-1/2,j) - F_{ad}^{x,c}(i+1/2,j)$$

$$+F_{ad}^{y,c}(i,j-1/2) - F_{ad}^{y,c}(i,j+1/2)$$
(3.2.17)

$$\hat{c}_{fct}^{i,j} = c_l^{i,j} + \frac{\Delta t}{\Delta x_i \Delta y_j \Delta z_{i,j}} \Delta c^{i,j}$$
(3.2.18)

The limiting procedure consists of the following four steps:

#### Sum all positive/negative antidiffusive fluxes at a cell

$$P_{i,j}^{+} = \max(0, F_{ad}^{x}(i-1/2, j)) + \max(0, -F_{ad}^{x}(i+1/2, j)) + \max(0, F_{ad}^{y}(i, j-1/2)) + \max(0, -F_{ad}^{y}(i, j+1/2)) P_{i,j}^{-} = \max(0, -F_{ad}^{x}(i-1/2, j)) + \max(0, F_{ad}^{x}(i+1/2, j)) + \max(0, -F_{ad}^{y}(i, j-1/2)) + \max(0, F_{ad}^{y}(i, j+1/2))$$

$$(3.2.19)$$

#### Define the maximum/minimum allowable antidiffusive flux at a cell

$$Q_{i,j}^{+} = \frac{V_{i,j}}{\Delta t} \left( c_{i,j}^{max} - c_{i,j}^{l} \right)$$

$$Q_{i,j}^{-} = \frac{V_{i,j}}{\Delta t} \left( c_{i,j}^{min} - c_{i,j}^{l} \right)$$
(3.2.20)

with the definition of  $c_{i,j}^{max}$  and  $c_{i,j}^{min}$ :

$$c_{i,j}^{max} = max \left( c_{i,j}^{l}, c_{i+1,j}^{l}, c_{i,j+1}^{l}, c_{i,j+1}^{l}, c_{i,j-1}^{l}, c_{i,j-1}^{l}$$

$$c_{i,j}^{min} = min\left(c_{i,j}^{l}, c_{i+1,j}^{l}, c_{i-1,j}^{l}, c_{i,j+1}^{l}, c_{i,j-1}^{l}, c_{i,j-1}^{l},$$

## Calculate the ratio of $Q_{i,j}^{\pm}$ and $P_{i,j}^{\pm}$

$$\begin{aligned} R_{i,j}^{+} &= \min\left(1, \frac{Q_{i,j}^{+}}{P_{i,j}^{+}}\right) if P_{i,j}^{+} \neq 0 \\ &= 0 if P_{i,j}^{+} = 0 \\ R_{i,j}^{-} &= \min\left(1, \frac{Q_{i,j}^{-}}{P_{i,j}^{-}}\right) if P_{i,j}^{-} \neq 0 \\ &= 0 if P_{i,j}^{-} = 0 \end{aligned}$$
(3.2.23)

**Define**  $T_{i+1/2,j}$  and  $T_{i,j+1/2}$ 

$$T_{i+1/2,j} = \min \begin{pmatrix} R_{i,j}^+, R_{i+1,j}^+ & if & F_{ad}^x(i+1/2,j) > 0\\ R_{i,j}^-, R_{i+1,j}^- & if & F_{ad}^x(i+1/2,j) > 0 \end{pmatrix}$$
(3.2.24)

**3.2.4.2.2 Slope Limiter** The upwinding scheme as defined in (3.2.12) is based on the assumption that the concentration within the donor cell is spatially constant. In fact the integrated FDM approach gives no direct indication of the innercell concentration distribution; only the average value is calculated.

The upwind scheme might be recalled in the framework of GODUNOV [24]. He suggested that hyperbolic problems should be solved by the explicit solution of RIEMANN problems in cells. For 1-D linear hyperbolic equations this can easily be done. The basic principle can be explained by three steps:

- Given cell-averaged data  $\{c_j^n\}$ , construct a function  $\tilde{c}(x, t_n)$ . (Piecewise constant in GODUNOV's method).
- Solve the conservation law exactly with this data to obtain  $\tilde{c}(x, t_{n+1})$ .
- Compute cell averages of the resulting solution to obtain  $\{c_i^{n+1}\}$ .

Fig. 3.4 illustrates this principle under the assumption of a constant concentration distribution. The black dots represent the average values at the previous time step, whereas the circles represent the average concentrations at the new time step.

From Fig. 3.4 it is obvious that the scheme gives the exact solution of the model problem for a COURANT number of unity. A COURANT number exceeding one would cause instabilities as information is only carried from one cell to its neighbouring cell. Any COURANT number less than unity leads to smeared solutions due to the averaging procedure. The total variation in an arbitrary subdomain decreases unless a boundary condition leads to new extrema. This total variation diminishing (TVD) property is a measure of the monotinicity of a scheme.



Figure 3.4: GODUNOV's method.

The flux between two nodes j - 1 and j integrated over a time step can be easily calculated from:

$$\mathcal{F}_{j-1,j} = v_{j-1,j} \Delta t c_{j-1}^n \tag{3.2.25}$$

The slope limiter approach is an extension of GODUNOV's method in which piecewise linear innercell distribution of concentration is assumed [67]. In order to achieve mass balance the local concentration at the cell centre must equal the average value. The scheme is illustrated in Fig. 3.5.

Defining a slope  $s_j$  within cell j, the time-integrated flux for this scheme is given by:

$$\mathcal{F}_{j-1,j} = v_{j-1,j} \Delta t \left( c_{j-1}^n + s_{j-1}^n \left( \frac{\Delta x_{j-1} - v_{j-1,j} \Delta t}{2} \right) \right)$$
(3.2.26)

The decisive factor in applying this method is the choice of the slope. Fig. 3.6 defines natural choices based on the concentration distribution. These may be calculated from:



Figure 3.5: Extension of GODUNOV's method under the assumption of a linear concentration distribution.



Figure 3.6: Definition of possible slopes for the slope limiter scheme.

$$s_{lin}^{dwn} = \frac{2(c_{j+1} - c_j)}{\Delta x_{j+1} + \Delta x_j}$$

$$s_{max}^{dwn} = \frac{2(c_{j+1} - c_j)}{\Delta x_j}$$

$$s_{lin}^{up} = \frac{2(c_j - c_{j-1})}{\Delta x_j + \Delta x_{j-1}}$$

$$s_{max}^{up} = \frac{2(c_j - c_{j-1})}{\Delta x_j}$$

$$(3.2.27)$$

Note that for the definition of upstream and downstream cells the subscripts are increase in the direction of flow. In the following figures a parameter  $\theta$  is adopted as a measure of the curvature of the concentration.  $\theta$  is given by:

$$\theta = \frac{s_{lin}^{up}}{s_{lin}^{dwn}} \tag{3.2.28}$$

#### Fig. 3.7 shows the defined slopes as a function of the curvature $\theta$ .



Figure 3.7: Defined slopes as a function of curvature.

Adopting  $s_{lin}^{dwn}$  as the slope is identical to the LAX-WENDROFF scheme whereas the application of  $s_{lin}^{up}$  leads to the BEAM-WARMING scheme. These two schemes are of second order accuracy. Any slope between these two can be assumed to be of second order. This region is shown in Fig. 3.8.


Figure 3.8: Second order region of slope limiters.

The TVD property of the entire scheme is obtained if the reconstruction is TVD [42]. This leads to the following limits:

- If a cell contains a local extremum, which is equivalent to  $\theta < 0$ , a constant innercell concentration distribution must be applied (s = 0).
- The reconstructed function must not lead to local concentrations outside the range of  $[c_{j-1}, c_{j+1}]$ . This is equivalent to  $|s| < min(|s_{max}^{dwn}|, |s_{max}^{up}|)$ .

This region is shown in Fig. 3.9. Hence a second order TVD region is given by the intersection of the second order region and the TVD region. This is shown in Fig. 3.10

In the following, four slope limiting procedures are presented which lie in the second order TVD region. The *minmod* slope limiter (see Fig. 3.11) follows the lower boundary of the second order TVD region, ROE's *Superbee* limiter [52] (see Fig. 3.12) follows the upper boundary of the second order TVD region, the front limiter (see Fig. 3.13) mainly follows the BEAM-WARMING line, and VAN LEER's limiter (see Fig. 3.14) is a smooth interpolation of upstream and downstream slopes.

The reconstruction of the *minmod* slope limiter is given by:

 $if \qquad s_{lin}^{dwn} \cdot s_{lin}^{up} < 0 \quad then \quad s = 0$   $elseif \quad |s_{lin}^{up}| < |s_{lin}^{dwn}| \quad then \quad s = s_{lin}^{up}$   $else \qquad \qquad s = s_{lin}^{dwn}$  (3.2.29)



Figure 3.9: TVD region of slope limiters.



Figure 3.10: Second order TVD region of slope limiters.



Figure 3.11: Definition of minmod slope limiter.



Figure 3.12: Definition of ROE's *Superbee* slope limiter.

The reconstruction of the ROE's *Superbee* limiter is given by:

$$\begin{array}{ll} if \qquad s_{lin}^{dwn} \cdot s_{lin}^{up} < 0 & then \quad s = 0 \\ elseif \qquad |s_{max}^{up}| < |s_{lin}^{dwn}| & then \quad s = s_{max}^{up} \\ elseif \qquad |s_{lin}^{dwn}| > |s_{lin}^{up}| & then \quad s = s_{lin}^{dwn} \\ elseif \qquad |s_{lin}^{up}| < |s_{max}^{dwn}| & then \quad s = s_{lin}^{up} \\ else & \qquad s = s_{max}^{dwn} \\ \end{array}$$

$$(3.2.30)$$



Figure 3.13: Definition of the HAEFNER's front limiter in the context of slope limiters.

The reconstruction of HAEFNER's front limiter is given by:

$$\begin{array}{ll} if \qquad s_{lin}^{dwn} \cdot s_{lin}^{up} < 0 \quad then \quad s = 0 \\ elseif \qquad |s_{lin}^{up}| < |s_{max}^{dwn}| \quad then \quad s = s_{lin}^{up} \\ else \qquad \qquad \qquad s = s_{max}^{dwn} \end{array}$$
(3.2.31)

A smooth limiter function is given by VAN LEER. For non-extrema he calculates the slope from the

harmonic mean of the linear upstream and downstream slopes:

Figure 3.14: VAN LEER's slope limiter as a function of curvature.

Note that the *minmod limiter*, the *Superbee* limiter and VAN LEER's limiter do not require the direction of flow for the reconstruction of the innercell concentration distribution, whereas the front limiter does. Fig. 3.15 illustrates the *minmod* slope limiter in an example.

In a semidiscrete version of the slope limiting approach the exact solution of the RIEMANN problem is replaced by a numerical integration scheme in time. This is an appropriate approach if the exact solution of the RIEMANN problem is difficult to obtain, namely in multidimensional problems and problems, in which advective transport is coupled to other processes. For a definite point in time the flux at an intercell boundary is given by:

$$F_{j-1,j,t} = v_{j_1,j,t}(c_{j-1,t} + s_{j-1,t}\Delta x_{j-1}/2)$$
(3.2.33)

The simpliest method of applying the scheme to multidimensional problems is to construct slopes for each direction independently in the semidiscrete context. For a correct explicit solution a bilinear approach would be necessary.

Note that all slope limiter schemes are nonlinear, as the choice of the interpolation is dependent on the solution in a nonlinear way. In contrast to the FCT algorithm, the slope limiter fits into the concept of



Figure 3.15: Spatial approximation of concentrations in upwind scheme (above) and under application of the *minmod* slope limiter scheme (below)

the method of lines (MOL). In the semidiscrete version it has no influence on any time discretization scheme, provided they are of second order accuracy, but it does require linearization.

The approach can be extended to higher order reconstruction. In order to achieve mass balance in the cells this requires interpolation of primitive functions, which are spatial integrals. The class of essentially non-oscillatory (ENO) schemes, developed by HARTEN ET AL. [25] follows this approach.

A test of all slope limiters described above is documented in section 3.6.1. Recently, in CONTRACT-2, ROE's *Superbee* limiter was implemented in the semidiscrete form.

## **3.2.5** Discretization in Time

### 3.2.5.1 Finite Difference Approximation

In this classical approach integration in time is carried out by one-point integration based on linear interpolation. Linear interpolation between the time steps  $t_n$  and  $t_{n+1}$  first must be applied to concentrations, mass fluxes and reactive sources/sinks:

$$c_{i,j}(t) = (1 - \Theta)c_{i,j}(t_n) + \Theta c_{i,j}(t_{n+1})$$

$$J_{i\pm 1/2,j\pm 1/2}^{x,y}(t) = (1 - \Theta)J_{i\pm 1/2,j\pm 1/2}^{x,y}(t_n) + \Theta J_{i\pm 1/2),j\pm 1/2}^{x,y}(t_{n+1})$$

$$r_{i,j}(t) = (1 - \Theta)r_{i,j}(t_n) + \Theta r_{i,j}(t_{n+1})$$

$$t = t_n + \Theta (t_{n+1} - t_n)$$
(3.2.34)

Time derivatives can thus be approximated by:

$$\frac{\partial c_{i,j}}{\partial t} = \frac{\Delta c_{i,j}}{\Delta t} = \frac{c_{i,j}(t_{n+1}) - c_{i,j}(t_n)}{t_{n+1} - t_n}$$
(3.2.35)

Choosing a time point of collocation  $\Theta$  for the calculation of  $c_{i,j}(t)$ ,  $r_{i,j}(t)$  and  $J_{i\pm 1/2,j\pm 1/2}^{x,y}$  and applying this to (3.2.2) yields:

$$\begin{pmatrix} \frac{c_{i,j}(t_{n+1}) - c_{i,j}(t_n)}{t_{n+1} - t_n} - (1 - \Theta)r_{i,j}(t_n) - \Theta r_{i,j}(t_{n+1}) \end{pmatrix} n_e \Delta x_i \Delta y_j \Delta z_{i,j} \\
+ \left( (1 - \Theta)J_{i+1/2,j}^x(t_n) + \Theta J_{i+1/2,j}^x(t_{n+1}) - (1 - \Theta)J_{i-1/2,j}^x(t_n) - \Theta J_{i-1/2,j}^x(t_{n+1}) \right) \Delta y_j \Delta z_{i,j} \\
+ \left( (1 - \Theta)J_{i,j+1/2}^y(t_n) + \Theta J_{i,j+1/2}^y(t_{n+1}) - (1 - \Theta)J_{i,j-1/2}^y(t_n) - \Theta J_{i,j-1/2}^y(t_{n+1}) \right) \Delta x_i \Delta z_{i,j} = 0$$
(3.2.36)

If  $\Theta$  is chosen to be zero the time integration scheme is fully explicit. This is the simpliest way of integration as all spatial derivatives are calculated for the known solution of the previous time step.

Every (partially) explicit method requires that the COURANT- and NEUMANN- numbers do not exceed unity:

$$Cr = max \left( \frac{v_x \Delta t}{\Delta x}, \frac{v_y \Delta t}{\Delta y} \right)$$

$$Ne = \frac{Q_{in,out} \Delta t}{\Delta x \Delta y \Delta z}$$
(3.2.37)

If  $\Theta$  is chosen to be unity the time integration scheme is fully implicit. This yields the most stable solution. Fully implicit integration does not restrict the size of the time step.

In any (partially) implicit scheme a large system of linear equations must be solved. The related matrix is positive definite but non-symmetric.

## 3.2.5.2 Lax-Wendroff Scheme

The LAX-WENDROFF scheme was developed to achieve a higher order of consistence for fully explicit one-step integration of the hyperbolic PDE for pure advective transport. In order to transform time derivatives into spatial derivatives the following transformation rules are valid:

$$\frac{\partial c}{\partial t} + v_x \frac{\partial c}{\partial x} + v_y \frac{\partial c}{\partial y} = 0$$
(3.2.38)

$$\Rightarrow \frac{\partial}{\partial t} = -v_x \frac{\partial}{\partial x} - v_y \frac{\partial}{\partial y}$$
(3.2.39)

$$\Rightarrow \frac{\partial^2}{\partial t^2} = v_x^2 \frac{\partial^2}{\partial x^2} + 2v_x v_y \frac{\partial^2}{\partial x \partial y} + v_y^2 \frac{\partial^2}{\partial y^2}$$
(3.2.40)

Truncation error analysis of the advective transport equation gives the following second order error terms (see (3.5.145)):

$$e_{2} = +\frac{\Delta t}{2}\frac{\partial^{2}c}{\partial t^{2}} + \Theta\Delta t v_{x}\frac{\partial^{2}c}{\partial x\partial t} + \Theta\Delta t v_{y}\frac{\partial^{2}c}{\partial y\partial t}$$
  
$$= \left(\frac{1}{2} - \Theta\right)\Delta t \left(v_{x}^{2}\frac{\partial^{2}c}{\partial x^{2}} + 2v_{x}v_{y}\frac{\partial^{2}c}{\partial x\partial y} + v_{y}^{2}\frac{\partial^{2}c}{\partial y^{2}}\right)$$
(3.2.41)

(3.2.41) indicates that explicit time integration includes an antidiffusive error causing instabilities. Adding a correction term with an artificial diffusion of  $\underline{\underline{D}}_{corr}$  leads to second order accuracy for explicit time integration:

$$\frac{\partial c}{\partial t} + \nabla \cdot (\underline{v}c) - \nabla \cdot (\underline{D}_{corr} \nabla c) = 0$$
(3.2.42)

$$\underline{\underline{D}}_{corr} = \begin{bmatrix} \left(\frac{1}{2} - \Theta\right) \Delta t v_x^2 & \left(\frac{1}{2} - \Theta\right) \Delta t v_x v_y \\ \left(\frac{1}{2} - \Theta\right) \Delta t v_x v_y & \left(\frac{1}{2} - \Theta\right) \Delta t v_y^2 \end{bmatrix}$$
(3.2.43)

Note that the LAX-WENDROFF scheme is based on TAYLOR extension. TAYLOR extension requires continuity. Hence the LAX-WENDROFF scheme cannot be used to stabilise solutions in the proximity of discontinuities. Nevertheless, the LAX-WENDROFF scheme is an easy-to-apply improvement of standard FDM. The computational effort is quite low as the scheme is linear.

### 3.2.5.3 Predictor-Corrector Scheme

0

The basic idea of the predictor-corrector scheme is to achieve second order accuracy with fully explicit time integration. For this purpose the integration of one time step is split into two substeps. In a fully explicit predictor step an intermediate concentration  $\tilde{c}(t_{n+1})$  is calculated. In the corrector step fluxes are calculated based on the concentration at the previous time step  $c(t_n)$  as well as on the intermediate concentration  $\tilde{c}(t_{n+1})$ , and then averaged. This correction by the trapezoidal rule yields a fully explicit scheme if second order accuracy. In order to obtain of a more accurate intermediate concentration the LAX-WENDROFF scheme may be applied in the predictor step.

### 3.2.5.4 Method of Lines

The integrated finite difference approach described in the sections preceding section 3.2.5 includes only spatial discretization, time derivatives remain unchanged. The partial differential equation of transport is thus transformed to a large system of ordinary differential equations which may be solved by the methods described above or by any other scheme suitable for the integration of ordinary differential equations. (3.2.44) illustrates this principle: c are the continuous concentrations whereas  $\underline{\tilde{c}}$  is the vector of nodal concentrations derived from spatial discretization.

$$f\left(c,\frac{\partial c}{\partial t},\frac{\partial c}{\partial x}\right) \to \tilde{f}\left(\underline{\tilde{c}},\frac{\partial \underline{\tilde{c}}}{\partial t}\right)$$
(3.2.44)

Note that the FCT scheme does not comply with the MOL approach whereas all other spatial discretization schemes presented above do.

# 3.3 Finite Element Method

# 3.3.1 Spatial Discretization and Isoparametric Concept

Spatial discretization in the Finite Element Method (FEM) consists in deviding the domain of interest into a finite number of elements which are characterized by discrete nodes. Spatial coordinates as well as state variables of interest are defined at the nodes. These parameters are interpolated within the elemenets. As the same interpolation function is used to compute both geometric values and state variables this approach is termed isoparametric.

In the case of multi-component reactive transport the state variables of interest are the concentrations  $c_i$  and the reaction rates  $r_i(\underline{c})$ . Interpolation is achieved by applying the shape function  $\underline{\Omega}$ . The sum of all  $\underline{\Omega}$  contributions must be unity:

$$\frac{x}{c} = \Omega \underline{A} \qquad (3.3.45)$$

$$\frac{x}{c} = \Omega \underline{\hat{r}} \qquad (3.3.45)$$

$$\underline{\hat{r}} = \begin{bmatrix} \hat{n}_{1} & \hat{p}_{1} & \hat{n}_{1} \\ \hat{n}_{2} & \hat{p}_{2} & \hat{n}_{2} \\ \vdots & \vdots & \vdots \\ \hat{n}_{no} & \hat{y}_{nno} & \hat{n}_{no} \end{bmatrix}$$

$$\frac{\hat{L}}{c} = \begin{bmatrix} \hat{c}_{1} \\ \hat{c}_{2} \\ \vdots \\ \hat{c}_{nno} \end{bmatrix}$$

$$(3.3.46)$$

$$(3.3.47)$$

$$(3.3.48)$$

$$\hat{L} = \begin{bmatrix} \hat{c}_{1} \\ \hat{c}_{2} \\ \vdots \\ \hat{c}_{nno} \end{bmatrix}$$

$$(3.3.49)$$

$$(3.3.50)$$

$$\hat{L} = \begin{bmatrix} \hat{r}_{1} \\ \hat{r}_{2} \\ \vdots \\ \hat{r}_{nno} \end{bmatrix}$$

$$(3.3.51)$$

The spatial derivatives of the parameters of interest may be derived by multiplying the vector of nodal values by the gradient of the shape function:

$$\nabla c = (\nabla_x \underline{\Omega}) \, \underline{\hat{c}}$$

in which

$$\nabla_{x}\underline{\Omega} = \begin{bmatrix} \frac{\partial\Omega_{1}}{\partial x} & \frac{\partial\Omega_{2}}{\partial x} & \cdots & \frac{\partial\Omega_{n_{no}}}{\partial x} \\ \frac{\partial\Omega_{1}}{\partial y} & \frac{\partial\Omega_{2}}{\partial y} & \cdots & \frac{\partial\Omega_{n_{no}}}{\partial y} \\ \frac{\partial\Omega_{1}}{\partial z} & \frac{\partial\Omega_{2}}{\partial z} & \cdots & \frac{\partial\Omega_{n_{no}}}{\partial z} \end{bmatrix}$$
(3.3.52)

Reaction rates are calculated on the basis of nodal concentrations and are interpolated in the same way as concentrations:

$$\hat{r}_i = f(\hat{c}_i) \tag{3.3.53}$$

These assumptions for spatial approximation lead to the following formulation of the PDE on the basis of one element:

$$n_{e}R\underline{\Omega}\frac{\partial \hat{c}}{\partial t} + \underline{\Omega}\,\hat{c}q_{in} - S_{0}\frac{\partial h}{\partial t}\underline{\Omega}\,\hat{c} + n_{e}\underline{v}_{a}^{T}(\nabla_{x}\underline{\Omega})\hat{c} - n_{e}\nabla\cdot(\underline{D}\,(\nabla_{x}\underline{\Omega}))\hat{c} = n_{e}\underline{\Omega}\,\hat{r} + \underline{\Omega}c_{in}q_{in}$$
(3.3.54)

# 3.3.2 Method of Weighted Residuals

In general (3.3.54) will not be exactly solvable for every point within an element. A local error, the residual  $\varepsilon$ , will occur:

$$n_{e}R\underline{\Omega}\frac{\partial \hat{c}}{\partial t} + \underline{\Omega}\ \hat{c}q_{in} - S_{0}\frac{\partial h}{\partial t}\underline{\Omega}\ \hat{c} + n_{e}\underline{v}_{a}^{T}(\nabla_{x}\underline{\Omega})\hat{c} - n_{e}\nabla\cdot(\underline{D}\ (\nabla_{x}\underline{\Omega}))\hat{c} - n_{e}\underline{\Omega}\ \hat{r} - \underline{\Omega}c_{in}q_{Q} = \varepsilon$$

$$(3.3.55)$$

This residual is redistributed amongst the nodes of an element using the weighting function  $\phi$ :

$$\underline{\phi} = \begin{bmatrix} \phi_1 \\ \phi_2 \\ \vdots \\ \phi_{n_{no}} \end{bmatrix}$$
(3.3.56)

A basic requirement is that the weighted residual  $\phi \varepsilon$  integrated over the domain must equate to zero:

$$\int_{V} \underline{\phi} \varepsilon dV = \underline{0} \tag{3.3.57}$$

As the domain is divided into elements the integral in (3.3.57) is equal to the sum of all element integrals:

$$\int_{V} \underline{\phi} \varepsilon dV = \sum_{1}^{n_{el}} \int_{V_{el}} \underline{\phi} \varepsilon dV = \underline{0}$$
(3.3.58)

(3.3.55) and (3.3.57) thus lead to:

$$\left(n_{e}\int_{V}\underline{\phi}R\underline{\Omega}dV\right)\frac{\partial\hat{c}}{\partial t} + \left(\int_{V}\underline{\phi}q_{in}\underline{\Omega}dV - \int_{V}\underline{\phi}S_{0}\frac{\partial h}{\partial t}\underline{\Omega}dV + n_{e}\int_{V}\underline{\phi}\underline{\nabla}_{a}^{T}(\nabla_{x}\underline{\Omega})dV - n_{e}\int_{V}\underline{\phi}\nabla\cdot\left(\underline{D}\left(\nabla_{x}\underline{\Omega}\right)\right)dV\right)\hat{c} - n_{e}\int_{V}\underline{\phi}\nabla\cdot\left(\underline{D}\left(\nabla_{x}\underline{\Omega}\right)\right)dV\right)\hat{c} - \left(n_{e}\int_{V}\underline{\phi}\underline{\Omega}dV\right)\hat{r} - \int_{V}\underline{\phi}q_{in}c_{in}dV = 0$$
(3.3.59)

which is solvable. Note that the solution of (3.3.59) need not necessarily represent the most accurate solution as local errors with changing signs within an element can be cancelled out by the integration procedure.

# 3.3.3 Partial Integration and Weak Formulation

### 3.3.3.1 Weak Formulation of Diffusive Mass Flux

(3.3.59) includes second order spatial derivatives in the diffusion term. Hence linear shape functions cannot be applied directly to describe diffusion. Applying GREEN's theorem (partial integration across the element boundaries) makes it possible to transform one derivation from the shape to the weighting function:

$$\left(\int_{V} \underline{\phi} \nabla \cdot (\underline{\underline{D}} (\nabla_{x} \underline{\Omega})) \, dV\right) \underline{\hat{c}} =$$

$$\left(\int_{\Gamma} \underline{\phi} \underline{n}^{T} \underline{\underline{D}} (\nabla_{x} \underline{\Omega}) \, d\Gamma - \int_{V} (\nabla_{x} \underline{\phi}^{T})^{T} \underline{\underline{D}} (\nabla_{x} \underline{\Omega}) \, dV\right) \underline{\hat{c}}$$
(3.3.60)

Inserting (3.3.60) into (3.3.59) leads to the weak form for the diffusive mass flux:

$$\begin{pmatrix}
n_{e} \int_{V} R \underline{\phi} \underline{\Omega} dV \\
\frac{\partial \hat{c}}{\partial t} + \left( \int_{V} \underline{\phi} q_{in} \underline{\Omega} dV - \int_{V} \underline{\phi} S_{0} \frac{\partial h}{\partial t} \underline{\Omega} dV + n_{e} \int_{V} \underline{\phi} \underline{v}_{a}^{T} (\nabla_{x} \underline{\Omega}) dV \\
+ n_{e} \int_{V} (\nabla_{x} \underline{\phi}^{T})^{T} \underline{\underline{D}} (\nabla_{x} \underline{\Omega}) dV \\
\frac{\partial \hat{c}}{\partial t} = \left( n_{e} \int_{V} \underline{\phi} \underline{\Omega} dV \right) \underline{\hat{r}} + \int_{V} \underline{\phi} q_{in} c_{in} dV + \left( n_{e} \int_{\Gamma} \underline{\phi} \underline{n}^{T} \underline{\underline{D}} (\nabla_{x} \underline{\Omega}) d\Gamma \right) \underline{\hat{c}} \qquad (3.3.61)$$

The weak formulation may be interpretated as solving the integrated differential equation for the diffusive mass flux. The boundary mass fluxes which now occur need not be calculated for interior element boundaries, as mass conservation requires the sum over all weighted boundary mass fluxes of an interior node to equal zero. Only nodes on the boundary of the total domain would require integration of boundary mass fluxes. Setting the diffusive mass flux across the boundary of the domain to zero (NEUMANN boundary condition) makes integration of boundary fluxes uneccesary. This introduces an error which is acceptable at least for all cases dominated by advection.

A great advantage of the weak formulation is that even inaccurate spatial integration does not lead to errors in the mass balance of the total domain. This is true only for the weak part of the mass flux. The strongly treated advective mass flux has to be integrated very accurately. No balancing of mass fluxes occurs with boundary integrals.

## 3.3.4 Weak Formulation of Total Mass Flux

To overcome the strict requirements of accuracy for the advective mass flux integration a weak form of advective mass flux can be formulated. Here the original definition of advective mass flux (2.2.6) can be used; applying the chain rule is not necessary:

$$n_e \int_{V} \underline{\phi} \nabla \cdot (\underline{v}_a c) \, dV = \int_{\Gamma} \underline{\phi} \underline{n}^T \underline{v}_f c \, d\Gamma - n_e \int_{V} (\nabla_x \underline{\phi}^T)^T \underline{v}_a c \, dV$$
(3.3.62)

The boundary integral for interior nodes can again be neglected. On the domain boundaries the advective mass fluxes can be expressed by the product of the discharge across the boundary, which is a direct result of flow calculations, and the concentration of the inflow or outflow. In the case of inflow nodes this inflow concentration has to be specifies by the user as a boundary condition, whereas the outflow concentration is simply the concentration computed at the boundary node. This leads to the following element equation:

$$\begin{pmatrix}
n_{e} \int_{V} R \underline{\phi} \underline{\Omega} dV \\
\frac{\partial \hat{c}}{\partial t} \\
+ \left( -n_{e} \int_{V} (\nabla_{x} \underline{\phi}^{T})^{T} \underline{v}_{a} \underline{\Omega} dV + \int_{\Gamma_{out}} \underline{\phi} \underline{n}^{T} \underline{v}_{f} \underline{\Omega} d\Gamma + n_{e} \int_{V} (\nabla_{x} \underline{\phi}^{T})^{T} \underline{\underline{D}} (\nabla_{x} \underline{\Omega}) dV \right) \hat{c} \qquad (3.3.63)$$

$$= \left( n_{e} \int_{V} \underline{\phi} \underline{\Omega} dV \right) \underline{\hat{r}} - \int_{\Gamma_{in}} \underline{\phi} \underline{n}^{T} \underline{v}_{f} c_{in} d\Gamma + \left( n_{e} \int_{\Gamma} \underline{\phi} \underline{n}^{T} \underline{\underline{D}} (\nabla_{x} \underline{\Omega}) d\Gamma \right) \underline{\hat{c}}$$

# 3.3.5 Transformation of Coordinates

The FEM formulations of (3.3.61) and (3.3.63) include spatial derivatives of shape and weighting functions as well as spatial integration of the expressions in total. These operations are carried out element by element. The transformation of coordinates permits a generalized calculation of derivatives, thus leading to easy-to-handle program codes. By introducing local coordinates  $s_1, s_2, s_3$  the following holds for a one-dimensional element:

$s_1 = +1$	$\underline{x} = \underline{x}_1$	
$s_1 = -1$	$\underline{x} = \underline{x}_2$	

a two-dimensional element:

$s_1$	=	+1	,	$s_2$	=	+1	<u>x</u>	=	$\underline{x}_1$
$s_1$	=	-1	,	$s_2$	=	+1	<u>x</u>	=	$\underline{x}_2$
$s_1$	=	-1	,	$s_2$	=	-1	<u>x</u>	=	$\underline{x}_3$
$s_1$	=	+1	,	$s_2$	=	-1	<u>x</u>	$\equiv$	$\underline{x}_4$

(3.3.65)

### and a three-dimensional element:

$s_1$	=	+1	,	$s_2$	=	+1	,	$s_3$	=	+1	<u>x</u>	=	$\underline{x}_1$
$s_1$	=	-1	,	$s_2$	=	+1	,	$s_3$	=	+1	<u>x</u>	=	$\underline{x}_2$
$s_1$	=	-1	,	$s_2$	=	-1	,	$s_3$	=	+1	<u>x</u>	=	$\underline{x}_3$
$s_1$	=	+1	,	$s_2$	=	-1	,	$s_3$	=	+1	<u>x</u>	=	$\underline{x}_4$
$s_1$	=	+1	,	$s_2$	=	+1	,	$s_3$	=	-1	<u>x</u>	=	$\underline{x}_5$
$s_1$	=	-1	,	$s_2$	=	+1	,	$s_3$	=	-1	<u>x</u>	=	$\underline{x}_6$
$s_1$	=	-1	,	$s_2$	=	-1	,	$s_3$	=	-1	<u>x</u>	=	$\underline{x}_7$
$s_1$	=	+1	,	$s_2$	=	-1	,	$s_3$	=	-1	<u>x</u>	=	$\underline{x}_8$

.



Figure 3.16: Linear 1-D element.



Figure 3.17: Quadrilateral 2-D element.



Figure 3.18: Hexahedral 3-D element.

Spatial gradients can be transformed by the JACOBIAN matrix:

$$\underline{J} = \begin{bmatrix} \frac{\partial x}{\partial s_1} & \frac{\partial y}{\partial s_1} & \frac{\partial z}{\partial s_1} \\ \frac{\partial x}{\partial s_2} & \frac{\partial y}{\partial s_2} & \frac{\partial z}{\partial s_2} \\ \frac{\partial x}{\partial s_3} & \frac{\partial y}{\partial s_3} & \frac{\partial z}{\partial s_3} \end{bmatrix} = (\nabla_s \underline{\Omega}) \underline{A}$$
(3.3.67)

with

$$\nabla_{s}\underline{\Omega} = \begin{bmatrix} \frac{\partial\Omega_{1}}{\partial s_{1}} & \frac{\partial\Omega_{2}}{\partial s_{1}} & \cdots & \frac{\partial\Omega_{n_{no}}}{\partial s_{1}} \\ \frac{\partial\Omega_{1}}{\partial s_{2}} & \frac{\partial\Omega_{2}}{\partial s_{2}} & \cdots & \frac{\partial\Omega_{n_{no}}}{\partial s_{2}} \\ \frac{\partial\Omega_{1}}{\partial s_{3}} & \frac{\partial\Omega_{2}}{\partial s_{3}} & \cdots & \frac{\partial\Omega_{n_{no}}}{\partial s_{3}} \end{bmatrix}$$

(3.3.68)

The following transformation rules are valid:

$$\nabla_x \underline{\Omega} = \underline{J}^{-1} (\nabla_s \underline{\Omega}) \tag{3.3.69}$$

and

$$\int_{V} dV = \int_{-1}^{+1} \int_{-1}^{+1} \int_{-1}^{+1} \det\left(\underline{J}\right) ds_1 ds_2 ds_3$$
(3.3.70)

Tranformation of coordinates transforms degenerated elements into orthogonal elements which can be integrated much easier. For this purpose the shape function  $\underline{\Omega}$  is defined by linear, bilinear and trilinear functions:

$$\underline{\Omega}\Big|_{1D} = \left[\frac{1}{2}(1+s_1), \frac{1}{2}(1-s_1)\right]$$
(3.3.71)



Figure 3.19: Linear shape function.

$$\underline{\Omega}\Big|_{2D} = \begin{bmatrix} \frac{1}{4}(1+s_1)(1+s_2) \\ \frac{1}{4}(1-s_1)(1+s_2) \\ \frac{1}{4}(1-s_1)(1-s_2) \\ \frac{1}{4}(1+s_1)(1-s_2) \end{bmatrix}^T$$

(3.3.72)



Figure 3.20: Bilinear shape function for node 1.



Figure 3.21: Bilinear shape function for node 2.



Figure 3.22: Bilinear shape function for node 3.



Figure 3.23: Bilinear shape function for node 4.

 $\underline{\Omega}\Big|_{3D} = \begin{bmatrix} \frac{1}{8}(1+s_1)(1+s_2)(1+s_3) \\ \frac{1}{8}(1-s_1)(1+s_2)(1+s_3) \\ \frac{1}{8}(1-s_1)(1-s_2)(1+s_3) \\ \frac{1}{8}(1+s_1)(1-s_2)(1+s_3) \\ \frac{1}{8}(1+s_1)(1+s_2)(1-s_3) \\ \frac{1}{8}(1-s_1)(1+s_2)(1-s_3) \\ \frac{1}{8}(1-s_1)(1-s_2)(1-s_3) \\ \frac{1}{8}(1+s_1)(1-s_2)(1-s_3) \\ \frac{1}{8}(1+s_1)(1-s_2)(1-s_3) \end{bmatrix}$ (3.3.73)

The JACOBIAN matrix  $\underline{J}$  is itself a function of local coordinates. This leads to the problem of direct integration of quadrilateral and hexagonal elements. The finite element formulation for an element (3.3.63) can now be expressed by:

$$\begin{pmatrix}
n_{e} \int_{-1}^{+1} \int_{-1}^{+1} R \underline{\phi} \underline{\Omega} \det(\underline{J}) ds_{1} ds_{2} ds_{3} \\
\frac{\partial \hat{c}}{\partial t} \\
+ \left(n_{e} \int_{-1}^{+1} \int_{-1}^{+1+1} \int_{-1}^{+1} (\nabla_{s} \underline{\phi}^{T})^{T} (\underline{J}^{-1})^{T} \underline{D} \underline{J}^{-1} (\nabla_{s} \underline{\Omega}) \\
- (\nabla_{s} \underline{\phi}^{T})^{T} (\underline{J}^{-1})^{T} \underline{v}_{a} \underline{\Omega} \det(\underline{J}) ds_{1} ds_{2} ds_{3} - \underline{\tilde{Q}}_{out} \right) \hat{c} \\
= \left(n_{e} \int_{-1}^{+1} \int_{-1}^{+1} \int_{-1}^{+1} +1 \underline{\phi} \underline{\Omega} \det(\underline{J}) ds_{1} ds_{2} ds_{3} \right) \hat{r} + \underline{\tilde{Q}}_{in} \hat{c}_{in} + \left(n_{e} \int_{\Gamma} \underline{\phi} \underline{n}^{T} \underline{D} (\nabla_{x} \underline{\Omega}) d\Gamma \right) \hat{c} \\$$
(3.3.74)

with

$$\underline{\tilde{Q}}_{in,out} = -\int_{\Gamma_{in,out}} \underline{\phi} \underline{n}^T \underline{v}_f \underline{\Omega} d\Gamma$$
(3.3.75)

The source-sink term for water flux  $\underline{\tilde{Q}}_{in,out}$  can be expressed by a diagonal matrix. For interior nodes it becomes a zero matrix. For nodes at the boundary of the domain the summation of all  $\underline{\tilde{Q}}_{in,out}$  terms at a node leads to the effective nodal inflow resulting from the flow calculation. The suffix in

denotes inflow boundaries ( $Q_{in,out} > 0$ ) while the suffix *out* denotes outflow boundaries ( $Q_{in,out} < 0$ ). Neglecting diffusive mass fluxes across boundaries leads to:

$$\begin{pmatrix}
n_{e} \int_{-1}^{+1} \int_{-1}^{+1} R \underline{\phi} \Omega \det(\underline{J}) ds_{1} ds_{2} ds_{3} \\
\frac{\partial \hat{c}}{\partial t} \\
+ \begin{pmatrix}
n_{e} \int_{-1}^{+1} \int_{-1}^{+1+1+1} (\nabla_{s} \underline{\phi}^{T})^{T} (\underline{J}^{-1})^{T} \underline{D} \underline{J}^{-1} (\nabla_{s} \Omega) \\
- (\nabla_{s} \underline{\phi}^{T})^{T} (\underline{J}^{-1})^{T} \underline{v}_{a} \Omega \det(\underline{J}) ds_{1} ds_{2} ds_{3} - \underline{\tilde{Q}}_{out} \\
\frac{\partial}{c} \\
= \begin{pmatrix}
n_{e} \int_{-1}^{+1+1+1+1} \int_{-1}^{+1} \underline{\phi} \Omega \det(\underline{J}) ds_{1} ds_{2} ds_{3} \\
n_{e} \int_{-1-1-1}^{+1+1+1} \int_{-1}^{+1} \underline{\phi} \Omega \det(\underline{J}) ds_{1} ds_{2} ds_{3} \\
\frac{\partial}{c} \\
\hat{r} + \underline{\tilde{Q}}_{in} \\
\frac{\partial}{c}_{in}
\end{cases}$$
(3.3.76)

# 3.3.6 Spatial Integration

For abitrary geometries the analytical solution of the integrals in (3.3.76) becomes rather complicated. Numerical integration by the GAUSSIAN quadrature method is a flexible alternative.

$$\int_{-1}^{+1} f(s)ds = 5/9f(0.7746) + 8/9f(0) + 5/9f(-0.7746)$$
(3.3.77)

# 3.3.7 Discretization in Time

### 3.3.7.1 Semidiscrete Formulation

In the semidiscrete formulation the FEM is applied only to spatial dimensions. Differentiation and integration with respect to time is performed by finite differences (FD). The scheme is equivalent to time integration as described in the FDM section.

Choosing a time point of collocation  $\Theta$  for the calculation of  $\underline{\hat{c}}(t)$  and  $\underline{\hat{r}}(t)$  leads to (3.3.78) for the weak formulation of diffusive mass flux and to (3.3.79) for the weak formulation of total mass flux:

$$\begin{pmatrix}
n_{e} \int_{V} R \underline{\phi} \underline{\Omega} dV \\
\frac{\hat{c}_{n+1}}{\Delta t} \\
+ \left( \int_{V} \underline{\phi} q_{in} \underline{\Omega} dV - \int_{V} \underline{\phi} S_{0} \frac{\partial h}{\partial t} \underline{\Omega} dV + n_{e} \int_{V} \underline{\phi} \underline{\mu}_{a}^{T} (\nabla_{x} \underline{\Omega}) dV \\
+ n_{e} \int_{V} (\nabla_{x} \underline{\phi}^{T})^{T} \underline{D} (\nabla_{x} \underline{\Omega}) dV \\
\theta \underline{\hat{c}}_{n+1} \\
- \left( n_{e} \int_{\Gamma} \underline{\phi} \underline{n}_{a}^{T} \underline{D} (\nabla_{x} \underline{\Omega}) d\Gamma \\
\theta \underline{\hat{c}}_{n+1} \\
= \left( n_{e} \int_{V} R \underline{\phi} \underline{\Omega} dV \\
\frac{\hat{c}_{n}}{\Delta t} \\
- \left( \int_{V} \underline{\phi} q_{in} \underline{\Omega} dV - \int_{V} \underline{\phi} S_{0} \frac{\partial h}{\partial t} \underline{\Omega} dV + n_{e} \int_{V} \underline{\phi} \underline{\mu}_{a}^{T} (\nabla_{x} \underline{\Omega}) dV \\
+ n_{e} \int_{V} (\nabla_{x} \underline{\phi}^{T})^{T} \underline{D} (\nabla_{x} \underline{\Omega}) dV \\
+ n_{e} \int_{V} (\nabla_{x} \underline{\phi}^{T})^{T} \underline{D} (\nabla_{x} \underline{\Omega}) dV \\
+ \left( n_{e} \int_{V} \underline{\phi} \underline{\Omega} dV \\
+ \int_{V} \underline{\phi} q_{in} c_{in} dV + \left( n_{e} \int_{\Gamma} \underline{\phi} \underline{n}^{T} \underline{D} (\nabla_{x} \underline{\Omega}) d\Gamma \\
\right) (1 - \Theta) \underline{\hat{c}}_{n}$$
(3.3.78)

$$\begin{pmatrix}
n_{e} \int_{V} R \underline{\phi} \underline{\Omega} dV \\
\frac{\hat{c}_{n+1}}{\Delta t} \\
+ \left( -n_{e} \int_{V} (\nabla_{x} \underline{\phi}^{T})^{T} \underline{v}_{a} \underline{\Omega} dV + \int_{\Gamma_{out}} \underline{\phi} \underline{n}^{T} \underline{v}_{f} \underline{\Omega} d\Gamma \\
+ n_{e} \int_{V} (\nabla_{x} \underline{\phi}^{T})^{T} \underline{D} (\nabla_{x} \underline{\Omega}) dV \\
\Theta \underline{\hat{c}}_{n+1} \\
- \left( n_{e} \int_{\Gamma} \underline{\phi} \underline{n}^{T} \underline{D} (\nabla_{x} \underline{\Omega}) d\Gamma \\
\right) \Theta \underline{\hat{c}}_{n+1} \\
= \left( n_{e} \int_{V} R \underline{\phi} \underline{\Omega} dV \\
\frac{\hat{c}_{n}}{\Delta t} \\
- \left( -n_{e} \int_{V} (\nabla_{x} \underline{\phi}^{T})^{T} \underline{v}_{a} \underline{\Omega} dV + \int_{\Gamma_{out}} \underline{\phi} \underline{n}^{T} \underline{v}_{f} \underline{\Omega} d\Gamma \\
+ n_{e} \int_{V} (\nabla_{x} \underline{\phi}^{T})^{T} \underline{D} (\nabla_{x} \underline{\Omega}) dV \\
+ \left( n_{e} \int_{V} \underline{\phi} \underline{\Omega} dV \\
\right) \underline{\hat{r}} - \int_{\Gamma_{in}} \underline{\phi} \underline{n}^{T} \underline{v}_{f} c_{in} d\Gamma + \left( n_{e} \int_{\Gamma} \underline{\phi} \underline{n}^{T} \underline{D} (\nabla_{x} \underline{\Omega}) d\Gamma \\
+ (1 - \Theta) \underline{\hat{c}}_{n} \\
+ \left( n_{e} \int_{V} \underline{\phi} \underline{\Omega} dV \\
\right) \underline{\hat{r}} - \int_{\Gamma_{in}} \underline{\phi} \underline{n}^{T} \underline{v}_{f} c_{in} d\Gamma + \left( n_{e} \int_{\Gamma} \underline{\phi} \underline{n}^{T} \underline{D} (\nabla_{x} \underline{\Omega}) d\Gamma \\
+ (1 - \Theta) \underline{\hat{c}}_{n} \\
\end{bmatrix}$$
(3.3.79)

With the definitions of (3.3.77) for spatial integration, (3.3.78) and (3.3.79) are linear systems of equations which can be solved using standard solvers.

### 3.3.7.2 Finite Elements in Space and Time

The transient transport equation (2.2.12) can be transformed into a steady-state equation in the spacetime continuum:

$$n_e \nabla \cdot (c\underline{v}_a^*) - n_e \nabla \cdot (\underline{D}^* \nabla c) - n_e r(c) = 0$$

with  $\underline{x}^{*} = \begin{bmatrix} x \\ y \\ z \\ t \end{bmatrix}$   $\underline{v}_{a}^{*} = \begin{bmatrix} v_{x} \\ v_{y} \\ v_{z} \\ 1 \end{bmatrix}$   $\underline{\underline{D}}^{*} = \begin{bmatrix} D_{xx} & D_{xy} & D_{xz} & 0 \\ D_{yx} & D_{yy} & D_{yz} & 0 \\ D_{zx} & D_{zy} & D_{zz} & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$ 

Application of the isoparametric concept and the method of weighted residuals is straightforward. The coordinates of the nodes now include time. Nodes of a space-time finite element differ both in space and time. Nodes may pr may not lie on discrete time layers while the spatial coordinates on different time layers relating to an element may or may not change. Various possible space-time distributions for one-dimensional elements in space are shown in Fig. 3.24.

Note that methods for the minimizing numerical errors for steady-state problems in space can easily be transformed for transient problems when space-time elements are applied. The computational effort is of course higher as integration of the elements now includes an additional dimension.

## 3.3.8 Minimization of Numerical Errors

### 3.3.8.1 Standard Galerkin Method

In the standard GALERKIN procedure the shape function and the weighting function are identical:

$$\phi = \underline{\Omega}^T$$

(3.3.80)



Figure 3.24: Classes of space-time elements.

The GALERKIN method has been shown to be an appropriate approach to solve parabolic and elliptic partial differential equations. In contrast to this the solution of hyperbolic PDE's by the standard GALERKIN method leads to instabilities. Applying the method of finite differences, similiar problems occur when central differentiation is applied. As a consequence, approaches comparable to FDM solutions have been developed for finite elements to overcome these shortcomings. For example, the LAX-WENDROFF method has been adapted to the TAYLOR-GALERKIN method while upwinding methods have led to inconsistent PETROV-GALERKIN schemes.

### 3.3.8.2 Artificial Longitudinal Diffusion

The diffusive/dispersive term in the transport equation is parabolic in character whereas the advective term is hyperbolic. Provided the resulting total PDE is sufficiently governed by diffusion no stability problems should occur. PERROCHET & BÉROD [49] developed a stability criterion based on amplification matrix analysis:

$$Pe_{app} \cdot Cr \le 2 \tag{3.3.82}$$

with the definition of the apparent PECLET number

$$Pe_{app} = \frac{\mid \underline{v}_a \mid \Delta x}{D_{app}} \tag{3.3.83}$$

and the COURANT number

$$Cr = \frac{|\underline{v}_a| \Delta t}{\Delta x} \tag{3.3.84}$$

With the definition of longitudinal dispersion  $D_l = \alpha_l | \underline{v}_a | + D_m$  (3.3.82) can be transformed into a minimum longitudinal dispersivity  $\alpha_l$  required for stability:

$$\alpha_l \ge \frac{|\underline{v}_a | \Delta t}{2} - \frac{D_m}{|\underline{v}_a |}$$
(3.3.85)

Note that this condition includes no evaluation of COURANT or PECLET numbers and can hence be easily applied to multidimenional systems.

#### 3.3.8.3 Taylor-Galerkin Method

DONEA [20] carried out a truncation error analysis of the GALERKIN solution for a pure hyperbolic partial differential equation of type (3.3.86):

$$\frac{\partial u}{\partial t} + A(u) = f \tag{3.3.86}$$

After some rearrangements the TAYLOR extension in a regular mesh leads to the following first and second truncation errors of the solution:

$$e_{1}(\Theta) = \Delta t \left[\frac{1}{2} - \Theta\right] \left(\frac{\partial f}{\partial t} - A(f) + A(A(u))\right)$$

$$e_{2}(\Theta) = \frac{1}{2}\Delta t^{2} \left[\frac{1}{3} - \Theta^{2}\right] \left(\frac{\partial^{2} f}{\partial t^{2}} - A\left(\frac{\partial f}{\partial t}\right) + A\left(A\left(\frac{\partial u}{\partial t}\right)\right)\right)$$

$$+ \frac{1}{2}\Delta t^{2} \left[\Theta - \Theta^{2}\right] \left(A\left(\frac{\partial f}{\partial t}\right) - A\left(A\left(\frac{\partial u}{\partial t}\right)\right)\right)$$
(3.3.87)

For the application in CONTRACT u, A and f are defined in the following way:

$$u := c$$

$$A(u) := \frac{1}{R} \underline{v}_a \nabla c$$

$$f := \frac{1}{R} r$$

$$(3.3.88)$$

with

$$\frac{\partial f}{\partial t} = 0 \tag{3.3.89}$$

within a time step. Substituting (3.3.88) and (3.3.89) into (3.3.87) thus leads to:

$$e_{1}(\Theta) = \frac{\Delta t}{R^{2}} \left[ \frac{1}{2} - \Theta \right] \left( \underline{v}_{a} \cdot \nabla r + \underline{v}_{a} \cdot \nabla \left( \underline{v}_{a} \cdot \nabla c \right) \right)$$

$$e_{2}(\Theta) = \frac{\Delta t^{2}}{2R^{2}} \left[ \frac{1}{3} - \Theta \right] \left( \underline{v}_{a} \cdot \nabla \left( \underline{v}_{a} \cdot \nabla \left( \frac{\partial c}{\partial t} \right) \right) \right)$$

$$(3.3.90)$$

Subtracting these errors leads to a solution scheme of second order accuracy in space and time. Diffusive mass fluxes are neglected. This simplification is justified since parabolic equations can be solved without stability problems by the GALERKIN procedure. As the two correction terms include second order spatial derivatives they have to be applied in a weak formulation. This results in the following scheme:

$$\begin{pmatrix}
n_{e} \int_{V} \underline{\phi} \Omega \, dV + n_{e} \frac{\Delta t^{2}}{2R^{2}} \left(\frac{1}{3} - \Theta\right) \int_{V} (\nabla_{x} \underline{\phi}^{T})^{T} \underline{v}_{a}^{T} \underline{v}_{a} (\nabla_{x} \Omega) \, dV \right) \frac{\partial \hat{c}}{\partial t} \\
+ \left(\int_{V} \underline{\phi} \frac{1}{R} q_{Q} \Omega \, dV - \int_{V} \underline{\phi} \frac{1}{R} S_{0} \frac{\partial h}{\partial t} \Omega \, dV + n_{e} \int_{V} \underline{\phi} \frac{1}{R} \underline{v}_{a}^{T} (\nabla_{x} \Omega) \, dV \\
+ n_{e} \int_{V} (\nabla_{x} \underline{\phi}^{T})^{T} \frac{1}{R} \underline{D} (\nabla_{x} \Omega) \, dV + n_{e} \frac{\Delta t}{R^{2}} \left(\frac{1}{2} - \Theta\right) \int_{V} (\nabla_{x} \underline{\phi}^{T})^{T} \underline{v}_{a}^{T} \underline{v}_{a} (\nabla_{x} \Omega) \, dV \right) \hat{c} \\
= \left(n_{e} \int_{V} \underline{\phi} \frac{1}{R} \Omega \, dV + n_{e} \frac{\Delta t}{R^{2}} \left(\frac{1}{2} - \Theta\right) \int_{V} \underline{\phi} \underline{v}_{a}^{T} (\nabla_{x} \Omega) \right) \hat{r} \\
+ \int_{V} \underline{\phi} \frac{1}{R} q_{Q} c_{in} \, dV + \left(n_{e} \int_{\Gamma} \underline{\phi} \underline{n}^{T} \frac{1}{R} \underline{D} (\nabla_{x} \Omega) d\Gamma \right) \hat{c} \\
\end{cases} \tag{3.3.91}$$

Similar to the LAX-WENDROFF scheme in the FDM the TAYLOR-GALERKIN method is only conditionally stable. Although it increases the order of consistency it will fail if discontinuities in the solution occur since TAYLOR expansion is only applicable to continuous functions.

The TAYLOR-GALERKIN method as described above was implemented in the transport code ROCK-FLOW-TM [40]. ROCKFLOW-TM is the kernel of CONTRACT-FEM.

### 3.3.8.4 Inconsistent Petrov-Galerkin Method

Applying the concept of upwind differnetiation to finite elements can be achieved by changing the weighting procedure in such a way that the advective terms have a greater influence on the downstream nodes than on upstream nodes. One possible way to realize this is to introduce a quadratic term into the linear weighting function for advection. The following additional requirements must be fulfilled:

- The quadratic term is positive for the downstream node and negative for the upstream node.
- The sum of all weighting functions is always unity.
- The integral of the quadratic term over the element should not exceed unity (full upwinding).

For the one-dimensional case this leads to:

$$\underline{\phi} = \begin{bmatrix} \frac{1}{2}(1+s) + \alpha \frac{3}{4}(1+s)(1-s) \\ \frac{1}{2}(1-s) - \alpha \frac{3}{4}(1+s)(1-s) \end{bmatrix}$$
(3.3.92)



Figure 3.25: Quadratic upwinding of linear elements.

where  $\alpha$  is the upwind coefficient ranging between -1 and +1 and is positiv if node 1 is the downstream node. Fig. 3.25 shows the graph of the weighting function.

The two-dimensional case can be developed by multiplying the 1-D weighting functions in both directions. Here an upwinding coefficient for each local direction has to be determined:

$$\underline{\phi} = \begin{bmatrix} \left(\frac{1}{2}(1+s_1) + \alpha_1\frac{3}{4}(1+s_1)(1-s_1)\right) & \left(\frac{1}{2}(1+s_2) + \alpha_2\frac{3}{4}(1+s_2)(1-s_2)\right) \\ \left(\frac{1}{2}(1-s_1) - \alpha_1\frac{3}{4}(1+s_1)(1-s_1)\right) & \left(\frac{1}{2}(1+s_2) + \alpha_2\frac{3}{4}(1+s_2)(1-s_2)\right) \\ \left(\frac{1}{2}(1-s_1) - \alpha_1\frac{3}{4}(1+s_1)(1-s_1)\right) & \left(\frac{1}{2}(1-s_2) - \alpha_2\frac{3}{4}(1+s_2)(1-s_2)\right) \\ \left(\frac{1}{2}(1+s_1) + \alpha_1\frac{3}{4}(1+s_1)(1-s_1)\right) & \left(\frac{1}{2}(1-s_2) - \alpha_2\frac{3}{4}(1+s_2)(1-s_2)\right) \end{bmatrix}$$
(3.3.93)

The upwinding procedure is only applied to the advection term whereas the diffusion term and the mass storage term remain the sames as in the standard GALERKIN formulation. Truncation error analysis for such an inconsistent upwinding procedure shows that artificial diffusion is introduced with a diffusion coefficient of  $\alpha v_a L/2$  in the one-dimensional case. If  $\alpha$  is optimally chosen this artificial diffusion balances out higher order truncation error terms.

**3.3.8.4.1** Streamline Orientation The artificial diffusion introduced by upwinding is required only in the direction of advective mass flux, which coincides with the direction of streamlines. Defining an arbitrary combination of upwinding coefficients  $\alpha_1$  to  $\alpha_{n_{dimen}}$  in multidimensional systems would lead to artificial diffusion perpendicular to the streamlines, or so-called *crosswind* diffusion. An incorrect assumption of transverse dispersivity leads to more significant errors as it is generally much smaller than longitudinal dispersivity. Hence upwinding in the local coordinates of a multidimensional element has to be balanced in the direction of streamlines.

Assuming an upwind coefficient in the direction of the streamline  $\alpha_0$ , projection in the direction of



Figure 3.26: Quadratic upwinding of bilinear elements.  $\alpha_{s_1}=\alpha_{s_2}=1.$  Node 1.



Figure 3.27: Quadratic upwinding of bilinear elements.  $\alpha_{s_1}=\alpha_{s_2}=1.$  Node 2.



Figure 3.28: Quadratic upwinding of bilinear elements.  $\alpha_{s_1} = \alpha_{s_2} = 1$ . Node 3.



Figure 3.29: Quadratic upwinding of bilinear elements.  $\alpha_{s_1}=\alpha_{s_2}=1.$  Node 4.

local coordinates leads to an upwind scheme free of crosswind diffusion:

$$\alpha_i = \alpha_0 \, \frac{\underline{v}_a \cdot \underline{e}_i}{|\,\underline{v}_a\,|} \tag{3.3.94}$$

In (3.3.94)  $\alpha_i$  is the upwind coefficient in the direction of the local coordinate  $s_i$  and  $\underline{e}_i$  is the related unit vector expressed in global coordinates. This projection can be calculated at every integration point inside the element. Alternatively  $\alpha_i$  can be evaluated at the edges of the element and interpolated over the element [26]. Methods to select upwind coefficients will be discussed below.

### 3.3.8.5 Galerkin Least Square Method

The method of least squares is defined by the following procedure: choose concentrations at the nodes of an element in such a way that the square of the residual integrated over the element is a minimum:

$$\underline{\hat{c}} \quad \int_{\tilde{V}} \varepsilon^2(\underline{\hat{c}}) dV = \min$$
(3.3.95)

Under the assumption that the general extremum condition is sufficient to fulfill (3.3.93), the condition simplifies to: the integrated square of residual partially derived with respect to the nodal concentrations is a zero vector. Applying the isoparametric concept to the latter leads to:

$$\frac{\partial}{\partial \hat{\underline{c}}} \int_{\tilde{V}} \varepsilon^{2}(\hat{\underline{c}}) dV = \underline{0}$$

$$\frac{\partial}{\partial \hat{\underline{c}}} \int_{\tilde{V}} (\mathcal{L}(\underline{\Omega} \ \hat{\underline{c}}))^{2} dV = \underline{0}$$

$$2 \int_{\tilde{V}} \left( \frac{\partial \mathcal{L}(\underline{\Omega} \ \hat{\underline{c}})}{\partial \hat{\underline{c}}} \right) \mathcal{L}(\underline{\Omega} \ \hat{\underline{c}}) dV = \underline{0}$$
(3.3.96)

in which  $\mathcal{L}$  is the differential operator describing the process of interest. (3.3.95) is the definition of the Finite Element Least Square (FELS) method. Prooving that the general extremum condition really satisfies (3.3.95) is not straightforward. Indeed ZINKIEVIC and TAYLOR noted, that the FELS solution is only conditional stable.

If the differential operator is a linear expression of the concentration the first term in the integral can be simplified to  $\mathcal{L}(\underline{\Omega})$ . Applying FELS to the advection-diffusion-reaction equation requires a full (space-time) finite element approximation quadratic in space and linear in time.

The GALERKIN Least Square method (GLS) developed by HUGHES ET AL. [35] is a linear combination of the GALERKIN method and the FELS method:

$$\int_{t_0}^{t_1} \int_{V} \underline{\Omega}^T \mathcal{L}(\underline{\Omega}\hat{c}) + \tau \frac{\partial \mathcal{L}(\underline{\Omega}\hat{c})}{\partial \underline{\hat{c}}} \mathcal{L}(\underline{\Omega}\hat{c}) dV dt = \underline{0}$$
(3.3.97)

The first factor of the least square part can also be interpreted as perturbation of the weighting function, thus leading to a PETROV-GALERKIN scheme. Substituting the definition of the differential operator for the advection-diffusion-reaction equation (2.2.13) into (3.3.96) leads to:

$$\begin{pmatrix} n_e \int_{t_0}^{t_1} \int_{V} R\underline{\phi} \frac{\partial \underline{\Omega}}{\partial t} dV dt + n_e \int_{t_0}^{t_1} \int_{V} \underline{\phi} \underline{v}_a^T (\nabla_x \underline{\Omega}) dV dt \\ + n_e \int_{t_0}^{t_1} \int_{V} (\nabla_x \underline{\phi}^T)^T \underline{\underline{D}} (\nabla_x \underline{\Omega}) dV dt \end{pmatrix} \underline{\hat{c}} \\ = \left( n_e \int_{t_0}^{t_1} \int_{V} \underline{\phi} \underline{\Omega} dV dt \right) \underline{\hat{r}} + \left( n_e \int_{t_0}^{t_1} \int_{\Gamma} \underline{\phi} \underline{n}^T \underline{\underline{D}} (\nabla_x \underline{\Omega}) d\Gamma dt \right) \underline{\hat{c}}$$

with

$$\underline{\phi} = \underline{\Omega}^{T} + \tau \left( n_{e} R \frac{\partial \underline{\Omega}}{\partial t} + n_{e} \underline{v}_{a}^{T} (\nabla_{x} \underline{\Omega}) - n_{e} \nabla \cdot (\underline{D} (\nabla_{x} \underline{\Omega})) - n_{e} \underline{\Omega} \frac{\partial r}{\partial c} \right)^{T}$$
(3.3.98)

Quadratic approximation in space is only necessary for the least square part of the diffusion term. As the diffusion equation can be solved quite accurately by the standard GALERKIN method, linear approximation in space is assumed to be sufficient. For a semidiscrete formulation in time the time derivative of the shape function vanishes. Furthermore, the reactive source/sink term r will now be treated as being independent of concentration. This leads to the definition of the Streamline Upwind PETROV-GALERKIN (SUPG) [6, 64] method:

$$\begin{pmatrix}
n_{e} \int_{V} R \underline{\phi} \underline{\Omega} dV \\
\frac{\hat{c}(t_{1}) - \hat{c}(t_{0})}{\Delta t} \\
+ \left(n_{e} \int_{V} \underline{\phi} \underline{v}_{a}^{T}(\nabla_{x} \underline{\Omega}) dV + n_{e} \int_{V} (\nabla_{x} \underline{\phi}^{T})^{T} \underline{D} (\nabla_{x} \underline{\Omega}) dV \right) (\Theta \hat{c}(t_{1}) + (1 - \Theta) \hat{c}(t_{0})) \quad (3.3.99) \\
= \left(n_{e} \int_{V} \underline{\phi} \underline{\Omega} dV \right) \hat{\underline{r}} + \left(n_{e} \int_{\Gamma} \underline{\phi} \underline{n}^{T} \underline{D} (\nabla_{x} \underline{\Omega}) d\Gamma \right) (\Theta \hat{c}(t_{1}) + (1 - \Theta) \hat{c}(t_{0}))$$

with

$$\underline{\phi} = \underline{\Omega}^T + \tau \left( n_e \underline{v}_a^T (\nabla_x \underline{\Omega}) \right)^T$$
(3.3.100)

 $\tau$  can be interpreted as an upwind coefficient which must be determined by stability considerations or truncation error analysis.  $\tau$  and the upwind coefficient  $\alpha$  of the inconsistent PETROV-GALERKIN method are related by:

$$\tau = \alpha \frac{h}{2n_e |\underline{v}_a|} \tag{3.3.101}$$

)



Figure 3.30: Weighting function in the SUPG scheme.

in which h is a measure of the element size, being identical to the element length in 1-D.

The SUPG method introduces an upwinding term oriented along the characteristics of advective transport at the collocation time point whereas the GLS method for a shape function at least quadratic in space and linear in time introduces an upwinding term oriented at the characteristics of total mass flux in a space-time domain. In contrast to the inconsistent upwinding, SUPG and GLS apply the perturbated weighting function to all terms of the partial differential equation. As can be shown by truncation error analysis this consistent formulation prevents the introduction of artificial diffusion.

### 3.3.8.6 Choice of the Upwind Coefficient

**3.3.8.6.1** Superconvergent steady-state solution in 1-D The key task in all upwind methods is to select an appropriate upwind coefficient  $\alpha_0$  or  $\tau$ . An overestimation of  $\alpha_0$  leads to artificial diffusion whereas an underestimation may lead to remaining instabilities. For one-dimensional steady-state problems without sink or source terms a nodally exact solution is given by HUGHES & BROOKS [1979] (3.3.102).

$$\alpha_{opt} = \coth\left(\frac{Pe}{2}\right) - \frac{2}{Pe} \approx \sqrt{\frac{Pe^2}{36 + Pe^2}}$$
(3.3.102)

A plot of (3.3.102) is shown in Fig. 3.31.

An extension of (3.3.102) to multidimensional and transient problems based on semidiscrete FEM formulations is not straightforward. The solutions developed below suffer either from artificial diffusion or instability or both.

**3.3.8.6.2** Extension to multidimensional problems The PECLET number required for application of (3.3.102) is defined in (3.3.83) for one-dimensional systems. A multidimensional definition



Figure 3.31: Dependency of upwind coefficient  $\alpha$  on the PECLET number.

might be obtained by transforming the seepage velocity and the dispersion tensor into local coordinates:

$$\underline{\underline{v}}_{loc} = \underline{\underline{J}}^{-1} \underline{\underline{v}}_{a}$$

$$\underline{\underline{D}}_{loc} = \underline{\underline{J}}^{-1} \underline{\underline{J}}^{-1} \underline{\underline{D}}$$
(3.3.103)

Note that the transformed velocity and dispersion tensor are already related to a length scale of the element by multiplication with the inverse JACOBIAN matrix. Hence the definition of the SUPG-related upwind factor  $\tau$  in (3.3.101) can be simplified to:

$$\tau = \frac{\alpha}{2n_e |\underline{v}_{loc}|} \tag{3.3.104}$$

For the definition of a multidimensional PECLET number a reduction of the parameters to scalar values is required. For this purpose the dispersion tensor in local coordinates is projected along the direction of velocity in local coordinates, thus leading to the following form of longitudinal dispersion in local coordinates:

 $\underline{e}_{v_{loc}} = \frac{1}{|\underline{v}_{loc}|} \underline{v}_{loc}$   $\delta_{loc} = \underline{e}_{v_{loc}}^T \underline{D}_{loc} \underline{e}_{v_{loc}}$ (3.3.105)

The resulting PECLET number is:

$$Pe = 2 \frac{|\underline{v}_{loc}|}{\delta_{loc}}$$
(3.3.106)

The factor 2 in (3.3.106) is a consequence of the definition of local coordinates from -1 to +1. Since the inverse JACOBIAN matrix transforms the length of the element edges to 2, this factor has to be included in (3.3.106). Note that in the publications of HUGHES and his working group a PECLET number is applied which does not include this factor. The PECLET number given by (3.3.106) can directly be applied in (3.3.102).

**3.3.8.6.3 Extension to transient problems** The steady-state case as discussed previously can be viewed as the worst case for transient problems. Hence the choice of an upwind coefficient for transient problems will never exceed  $\alpha_{opt}$  as defined for the related steady-state problem. Minimizing artificial diffusion will necessitate assumptions aimed at decreasing alpha as a function of the COURANT number. This can be done

- either by defing a PECLET number for space-time elements, as the transient case simplifies to a steady-state problem in full finite element discretization,
- or by defining an upwind coefficient based on stability analysis for semidiscrete formulations.

For the second approach NOORISHAD ET AL. [47] developed the following relationship:

$$\alpha_{opt} = Cr - \frac{2}{Pe} \tag{3.3.107}$$

(3.3.107) is based on the same stability criterion as (3.3.85) and leads to identical results at least for 1-D problems.

### 3.3.8.7 Localized Adjoint Method

**3.3.8.7.1 General Approach** Assuming that the advection-dispersion-reaction equation has a linear decay expression on the left-hand side of the equation and zeroth order source/sink terms on the right-hand side:

$$\mathcal{L}(c) = \frac{\partial c}{\partial t} + \nabla \cdot (\underline{v}_a c) - \nabla \cdot (\underline{\underline{D}} \nabla c) + \lambda c = r$$
(3.3.108)

a general weak formulation can be achieved by introducing a weighting or test function  $\phi$  in the space-time domain:

$$\int_{t_n}^{t_{n+1}} \int_{V} \phi \mathcal{L}(c) \, dV dt = \int_{t_n}^{t_{n+1}} \int_{V} \phi r \, dV dt$$

$$\int_{t_n}^{t_{n+1}} \int_{V} \phi \left( \frac{\partial c}{\partial t} + \nabla \cdot (\underline{v}_a c) - \nabla \cdot (\underline{\underline{D}} \nabla c) + \lambda c \right) \, dV dt = \int_{t_n}^{t_{n+1}} \int_{V} \phi r \, dV dt$$
(3.3.109)

Applying GREEN's theorem to the time derivative in the time direction and to the advective-dispersive terms in the spatial direction leads to:

$$-\int_{t_{n+1}}^{t_{n+1}} \int_{V} \frac{\partial \phi}{\partial t} c \, dV dt + \int_{V} \phi c \left(t_{n+1}\right) \, dV - \int_{V} \phi c \left(t_{n}\right) \, dV$$

$$-\int_{t_{n+1}}^{t_{n+1}} \int_{V} \nabla \phi \cdot \underline{v}_{a} c \, dV dt + \int_{t_{n+1}}^{t_{n+1}} \int_{V} \phi \underline{n} \cdot \underline{v}_{a} c \, d\Gamma dt$$

$$+\int_{t_{n}}^{t_{n+1}} \int_{V} \nabla \phi \cdot \left(\underline{D} \nabla c\right) \, dV dt - \int_{t_{n}}^{t_{n+1}} \int_{V} \phi \underline{n} \cdot \left(\underline{D} \nabla c\right) \, d\Gamma dt \qquad (3.3.110)$$

$$+\int_{t_{n}}^{t_{n+1}} \int_{V} \phi \lambda c \, dV dt$$

$$=\int_{t_{n}}^{t_{n+1}} \int_{V} \phi r \, dV dt$$

A second application of GREEN's theorem to the dispersive term yields:

$$- \int_{t_{n-1}}^{t_{n+1}} \int_{V} \frac{\partial \phi}{\partial t} c \, dV dt + \int_{V} \phi c (t_{n+1}) \, dV - \int_{V} \phi c (t_{n}) \, dV$$

$$- \int_{t_{n-1}}^{t_{n+1}} \int_{V} \nabla \phi \cdot \underline{v}_{a} c \, dV dt + \int_{t_{n+1}}^{t_{n+1}} \int_{\Gamma_{V}} \phi \underline{n} \cdot \underline{v}_{a} c \, d\Gamma dt$$

$$- \int_{t_{n}}^{t_{n+1}} \int_{V} \nabla \cdot \left(\underline{D}^{T} \nabla \phi\right) c \, dV dt - \int_{t_{n}}^{t_{n+1}} \int_{\Gamma_{V}} \phi \underline{n} \cdot \left(\underline{D} \nabla c\right) \, d\Gamma dt$$

$$+ \int_{t_{n-1}}^{t_{n+1}} \int_{V} \phi \lambda c \, dV dt$$

$$= \int_{t_{n}}^{t_{n+1}} \int_{V} \phi r \, dV dt$$
(3.3.111)

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$$\int_{t_{n}}^{t_{n+1}} \int_{V} \mathcal{L}^{*}(\phi)c \, dV dt + \int_{V} \phi c(t_{n+1}) \, dV - \int_{V} \phi c(t_{n}) \, dV + \int_{V} \int_{t_{n+1}}^{t_{n+1}} \int_{\Gamma_{V}} \phi \underline{n} \cdot \underline{v}_{a} c \, d\Gamma dt + \int_{t_{n}}^{t_{n+1}} \int_{\Gamma_{V}} \phi \underline{n} \cdot \left(\underline{\underline{D}} \nabla c\right) \, d\Gamma dt + \int_{t_{n}}^{t_{n+1}} \int_{\Gamma_{V}} \left(\underline{\underline{D}}^{T} \nabla \phi\right) \cdot \underline{n} c \, d\Gamma dt \\ = \int_{t_{n}}^{t_{n+1}} \int_{V} \phi r \, dV dt$$
(3.3.112)

in which  $\mathcal{L}^*$  is the adjoint operator of the partial differential equation. Evaluation of inner integrals in space-time elements on the right-hand side of (3.3.112) becomes unnecessary for all test functions fulfilling  $\mathcal{L}^*(\phi) = 0$ :

$$\mathcal{L}^*(\phi) = -\frac{\partial\phi}{\partial t} - \nabla\phi \cdot \underline{v}_a - \nabla \cdot \left(\underline{\underline{D}}^T \nabla\phi\right) + \lambda\phi = 0$$
(3.3.113)

In the localized adjoint method (LAM) test functions locally fulfilling (3.3.113) are applied. In the following two sections a space-time approach and a semidiscrete approach will be discussed.

**3.3.8.7.2 Space-Time LAM** The boundary integral of the advective terms in (3.3.112) vanishes if the space-time boundaries of the elements follow characeristics of advective transport. This leads to the Eulerian-Langrangian localized adjoint method (ELLAM) introduced by CELIA ET AL. [11]:

$$\int_{V} \phi c(t_{n+1}) \, dV - \int_{V} \phi c(t_{n}) \, dV$$

$$- \int_{t_{n-\Gamma_{V}}}^{t_{n+1}} \int_{V} \phi \underline{n} \cdot \left(\underline{\underline{D}} \nabla c\right) \, d\Gamma dt + \int_{t_{n-\Gamma_{V}}}^{t_{n+1}} \int_{V} \left(\underline{\underline{D}}^{T} \nabla \phi\right) \cdot \underline{n} c \, d\Gamma dt$$

$$= \int_{t_{n}}^{t_{n+1}} \int_{V} \phi r \, dV dt$$
(3.3.114)

The choice of an optimal test function fulfilling (3.3.113) is straightforward in an EULERIAN-LA-GRANGIAN approach:

• In space the test function should be a polynomial of order zero or one leading to a finite volume formulation or a standard linear finite element formulation in space.

- In the space-time domain the test function should follow the characteristics of advective transport.
- An exponential increase with time with an exponent of  $\lambda t$  has to be introduced if linear decay is taken into account.

Fig. 3.32 and Fig. 3.33 show space-time elements and test functions for the one-dimensional case.



Figure 3.32: Space-time element linear in space.

The ELLAM approach directly indicates how boundary conditions should be handled since at boundaries the element edges can no longer follow characteristics and the boundary integrals for advective mass flux in (3.3.112) are to be evaluated. Furthermore, the scheme is perfectly mass conservative as, in contrast to other EULERIAN-LANGRANGIAN methods, spatial integrals over the entire spatial domain are developed from the spatial derivatives. Nevertheless, a number of disadvantages of all EULERIAN-LANGRANGIAN methods still remains:

- Accurate evaluation of the space-time boundary integrals for diffusive mass flux requires high computational effort. Operator split methods may be a valid simplification for advective-dominant transport but leads to time step restrictions.
- The source/sink term still has to be integrated over the entire space-time domain. Since source/ sink terms due to chemical interactions do not usually follow the characteristics, the evaluation



Figure 3.33: Space-time element constant in space.

of integrals again leads to high computational effort. Operator split methods for coupling of reactive terms to advective-dispersive transport circumvent this problem but should be handled with care.

- Boundary conditions lead to space-time boundary integrals which can be irregularly configurated in multidimensional applications.
- The backtracked nodes will not conincide in general with the nodes of spatial interpolation at the old time level. As a consequence, evaluation of the spatial integral at the old time level includes products of at least two hyperbolic paraboloids in the 2-D case. A test function which is constant in space will lead to less complications.
- Artificial diffusion produced by backtracking. Although adaptive mesh refinement can be included in the scheme, this again increases the computational effort.

**3.3.8.7.3** Semidiscrete LAM As a consequence of the problems listed above, semidiscrete methods should be viewed as simplified alternatives to the principally more accurate time-space approach. CELIA ET AL. [10] developed optimal test functions (OTF) based on LAM for semidicrete methods.

In this case only the spatial part of the localized adjoint operator has to be taken into account:

$$\mathcal{L}^*(\phi) = -\nabla\phi \cdot \underline{v}_a - \nabla \cdot \left(\underline{\underline{D}}^T \nabla\phi\right) + \lambda\phi = 0$$
(3.3.115)

The optimal choice of a test function fulfilling (3.3.115) corresponds to the solution, in which the boundary integrals of the advective mass flux vanish. Under the condition that the velocity is continuous, this leads to boundary conditions in which  $\phi$  is a constant (e.g. 1) at the node of interest and equals zero at the other node(s) of the element. In one dimension this yields:

$$\underline{\phi}(x) = \begin{bmatrix} \frac{EXP\left(-\frac{L\left(v+\tilde{v}\right)+x\left(v-\tilde{v}\right)}{2D}\right)-EXP\left(-\frac{L\left(v-\tilde{v}\right)+x\left(v+\tilde{v}\right)}{2D}\right)}{-EXP\left(-\frac{L\left(v-\tilde{v}\right)}{2D}\right)+EXP\left(-\frac{L\left(v+\tilde{v}\right)}{2D}\right)} \\ \frac{-EXP\left(-\frac{x\left(v-\tilde{v}\right)}{2D}\right)+EXP\left(-\frac{x\left(v+\tilde{v}\right)}{2D}\right)}{-EXP\left(-\frac{L\left(v-\tilde{v}\right)}{2D}\right)+EXP\left(-\frac{L\left(v+\tilde{v}\right)}{2D}\right)} \end{bmatrix}$$
(3.3.116)  
with  
$$\tilde{v} = \sqrt{v^{2}+4D\lambda}$$

Note that  $\tilde{v}$  equals v if no linear decay occurs. For this case (3.3.116) simplifies to:

$$\underline{\phi}(x) = \begin{bmatrix} \frac{e^{-Pe} - e^{-Pex/L}}{e^{-Pe} - 1} \\ \frac{e^{-Pex/L} - 1}{e^{-Pe} - 1} \end{bmatrix}$$
(3.3.117)

The resulting test function is illustrated in Fig. 3.34 for Pe=10.

Applying linear shape functions (3.3.117) leads to the following analytical integrals:

Mass matrix  $\underline{M}$ 

$$\underline{\underline{M}} = \frac{L}{2Pe^{2}(e^{-Pe}-1)} \begin{bmatrix} e^{-Pe}(Pe^{2}-2) + 2 - 2Pe & e^{-Pe}(2Pe + Pe^{2}+2) - 2\\ 2e^{-Pe} - Pe^{2} - 2 + 2Pe & e^{-Pe}(-2Pe - 2) - Pe^{2} + 2 \end{bmatrix}$$
(3.3.118)

Mobility matrix  $\underline{A}$ 

$$\underline{\underline{A}} = \frac{D}{L\left(e^{-Pe} - 1\right)} \begin{bmatrix} -e^{-Pe} + 1 - Pe & e^{-Pe}\left(Pe + 1\right) - 1\\ e^{-Pe} - 1 + Pe & -e^{-Pe}\left(Pe + 1\right) + 1 \end{bmatrix}$$
(3.3.119)



Figure 3.34: Optimal test function for semidiscrete LAM without linear decay (Pe=10).

#### 3.3.8.8 Finite Element Control Volume Approach

The GALERKIN and PETROV-GALERKIN methods described above do not preserve nodal mass balance. Mass balance is achieved only over the entire domain. This is due to the overlapping patch volumes of neighbouring nodes.

In the FEM Control Volume approach each element is divided into node-related subdomains. For each subdomain the integrated form of the transport equation (3.2.1) must be solved. In contrast to the Integrated Finite Difference approach, unstructured grids can be applied. For the evaluation of mass fluxes at the inner-element subdomain boundaries the shape function of the FEM approach is used.

For quadrilateral elements the subdomains can easily constructed by connecting the centres of opposite edges. This is illustrated in Fig. 3.36.

The shape function  $\underline{\Omega}$  of the auxiliary nodes I, II, III, IV and C is defined by:

$$\underline{\Omega}_{I} = \begin{bmatrix} 1/2 & , 1/2 & , 0 & , 0 \end{bmatrix}$$

$$\underline{\Omega}_{II} = \begin{bmatrix} 0 & , 1/2 & , 1/2 & , 0 \end{bmatrix}$$

$$\underline{\Omega}_{III} = \begin{bmatrix} 0 & , 0 & , 1/2 & , 1/2 \end{bmatrix}$$

$$\underline{\Omega}_{IV} = \begin{bmatrix} 1/2 & , 0 & , 0 & , 1/2 \end{bmatrix}$$

$$\underline{\Omega}_{C} = \begin{bmatrix} 1/4 & , 1/4 & , 1/4 & , 1/4 \end{bmatrix}$$
(3.3.120)



Figure 3.35: Definition of control volumes in 2-D.



Figure 3.36: Construction of control volumes in 2-D.

The mass matrix  $\underline{M}$  is diagonal and defined by the volumes of the four subdomains (3.3.121):

$$V_{el} = d_{el}n_{e} \left| \frac{1}{2}((x_{1} - x_{3})(y_{2} - y_{4}) - (y_{1} - y_{3})(x_{2} - x_{4})) \right|$$

$$\underline{M}_{FECV} = d_{el}n_{e} \left[ \begin{array}{c} A_{1} & 0 & 0 & 0 \\ 0 & A_{2} & 0 & 0 \\ 0 & 0 & A_{3} & 0 \\ 0 & 0 & 0 & A_{4} \end{array} \right]$$

$$A_{1} = \left| \frac{1}{16}((3x_{1} - x_{2} - x_{3} - x_{4})(y_{2} - y_{4}) - (3y_{1} - y_{2} - y_{3} - y_{4})(x_{2} - x_{4})) \right| \quad (3.3.121)$$

$$A_{2} = \left| \frac{1}{16}((-x_{1} + 3x_{2} - x_{3} - x_{4})(y_{3} - y_{1}) - (-y_{1} + 3y_{2} - y_{3} - y_{4})(x_{3} - x_{1})) \right|$$

$$A_{3} = \left| \frac{1}{16}((-x_{1} - x_{2} + 3x_{3} - x_{4})(y_{4} - y_{2}) - (-y_{1} - y_{2} + 3y_{3} - y_{4})(x_{4} - x_{2})) \right|$$

$$A_{4} = \left| \frac{1}{16}((-x_{1} - x_{2} - x_{3} + 3x_{4})(y_{1} - y_{3}) - (-y_{1} - y_{2} - y_{3} + 3y_{4})(x_{1} - x_{3})) \right|$$

The mobility matrix  $\underline{\underline{A}}$  may be partitioned into four rows:

$$\underline{\underline{A}} = d_{el} \begin{bmatrix} \underline{a}_1 \\ \underline{a}_2 \\ \underline{a}_3 \\ \underline{a}_4 \end{bmatrix}$$
(3.3.122)

The entries  $\underline{a}_1$  to  $\underline{a}_4$  can be evaluated from the fluxes across the inner-element subdomain boundaries:

$$\underline{a}_{1} = \underline{f}_{2,1} + \underline{f}_{4,1}$$

$$\underline{a}_{2} = -\underline{f}_{2,1} + \underline{f}_{3,2}$$

$$\underline{a}_{3} = -\underline{f}_{3,2} - \underline{f}_{3,4}$$

$$\underline{a}_{4} = \underline{f}_{3,4} - \underline{f}_{4,1}$$
(3.3.123)

The integral mass fluxes across the inner-element subdomain boundaries may be evaluated by twopoint integration. For this purpose the mass fluxes at the auxiliary points I, II, III, IV and C must be evaluated. (3.3.124) defines the fluxes across these boundaries:

$$\underline{f}_{2,1} = n_e L_{I,C} n_{\perp I,C}^T (\underline{j}_I + \underline{j}_C) / 2$$

$$\underline{f}_{3,2} = n_e L_{II,C} n_{\perp II,C}^T (\underline{j}_{II} + \underline{j}_C) / 2$$

$$\underline{f}_{3,4} = n_e L_{C,III} n_{\perp III,C}^T (\underline{j}_{III} + \underline{j}_C) / 2$$

$$\underline{f}_{4,1} = n_e L_{C,IV} n_{\perp IV,C}^T (\underline{j}_{IV} + \underline{j}_C) / 2$$
(3.3.124)

where  $L_{I,C}$  is the length of the innercell subdomain boundary between the auxiliary points I and Cand  $n_{\perp I,C}$  is the unit vector perpendicular to this boundary.  $n_{\perp I,C}$  is directed towards node 1,  $n_{\perp II,C}$ towards node 2,  $n_{\perp C,III}$  towards node 4 and  $n_{\perp C,IV}$  towards node 1.  $\underline{j}_P$  is the mass flux at point P, where P can be I, II, III, IV or C. (3.3.125) defines these fluxes under the application of central differentiation:

$$\underline{j}_P = \underline{v}_{a,P} \underline{\Omega}_P - \underline{D} (\nabla_x \Omega_P)$$
(3.3.125)

(3.3.126) gives the spatial gradient of the shape function  $\nabla_x \underline{\Omega}$  for any point  $(s_1, s_2)$  inside the element.

$$\nabla_{x}\Omega = \begin{bmatrix} \frac{\partial\Omega_{1}}{\partial x} & \frac{\partial\Omega_{2}}{\partial x} & \frac{\partial\Omega_{3}}{\partial x} & \frac{\partial\Omega_{4}}{\partial x} \\ \frac{\partial\Omega_{1}}{\partial y} & \frac{\partial\Omega_{2}}{\partial y} & \frac{\partial\Omega_{3}}{\partial y} & \frac{\partial\Omega_{4}}{\partial y} \end{bmatrix} \\
\frac{\partial\Omega_{1}}{\partial x} = (y_{2}(1+s_{2})+y_{3}(s_{1}-s_{2})-y_{4}(1+s_{1}))/\%1 \\
\frac{\partial\Omega_{2}}{\partial x} = (-y_{1}(1+s_{2})+y_{3}(1-s_{1})+y_{4}(s_{1}+s_{2}))/\%1 \\
\frac{\partial\Omega_{3}}{\partial x} = (-y_{1}(s_{1}-s_{2})-y_{2}(1-s_{1})+y_{4}(1-s_{2}))/\%1 \\
\frac{\partial\Omega_{4}}{\partial x} = (y_{1}(1+s_{1})-y_{2}(s_{1}+s_{2})-y_{3}(1-s_{2}))/\%1 \\
\frac{\partial\Omega_{1}}{\partial y} = (-x_{2}(1+s_{2})-x_{3}(s_{1}-s_{2})+x_{4}(1+s_{1}))/\%1 \\
\frac{\partial\Omega_{2}}{\partial y} = (x_{1}(1+s_{2})-x_{3}(1-s_{1})-x_{4}(s_{1}+s_{2}))/\%1 \\
\frac{\partial\Omega_{2}}{\partial y} = (-x_{1}(1+s_{1})+x_{2}(s_{1}+s_{2})+x_{3}(1-s_{2}))/\%1 \\
\frac{\partial\Omega_{4}}{\partial y} = (-x_{1}(1+s_{1})+x_{2}(s_{1}+s_{2})+x_{3}(1-s_{2}))/\%1 \\
\frac{\partial\Omega_{4}}{\partial y} = (x_{1}(y_{2}-x_{2}y_{1})(1+s_{2})+(x_{1}y_{3}-x_{3}y_{1})(s_{1}-s_{2})+(x_{4}y_{1}-x_{1}y_{4})(1+s_{1})+(x_{2}y_{3}-x_{3}y_{2})(1-s_{1})+(x_{2}y_{4}-x_{4}y_{2})(s_{1}+s_{2})+(x_{3}y_{4}-x_{4}y_{3})(1-s_{2})
\end{aligned}$$

For the point C with local coordinates (0,0), (3.3.126) simplifies to:

$$\frac{\partial \Omega_1}{\partial x} = (y_2 - y_4)/\%1$$

$$\frac{\partial \Omega_2}{\partial x} = (-y_1 + y_3)/\%1$$

$$\frac{\partial \Omega_3}{\partial x} = (-y_2 + y_4)/\%1$$

$$\frac{\partial \Omega_4}{\partial x} = (y_1 - y_3)/\%1$$

$$\frac{\partial \Omega_1}{\partial y} = (-x_2 + x_4)/\%1$$

$$\frac{\partial \Omega_2}{\partial y} = (x_1 - x_3)/\%1$$

$$\frac{\partial \Omega_3}{\partial y} = (x_2 - x_4)/\%1$$

$$\frac{\partial \Omega_4}{\partial y} = (-x_1 + x_3)/\%1$$

$$\%1 = x_1y_2 - x_2y_1 + x_4y_1 - x_1y_4 + x_2y_3 - x_3y_2 + x_3y_4 - x_4y_3$$

For the point I with local coordinates (0,1), (3.3.126) simplifies to:

$$\frac{\partial\Omega_1}{\partial x} = (2y_2 - y_3 - y_4)/\%1$$

$$\frac{\partial\Omega_2}{\partial x} = (-2y_1 + y_3 + y_4)/\%1$$

$$\frac{\partial\Omega_3}{\partial x} = (y_1 - y_2)/\%1$$

$$\frac{\partial\Omega_4}{\partial x} = (y_1 - y_2)/\%1$$

$$\frac{\partial\Omega_1}{\partial y} = (-2x_2 + x_3 + x_4)/\%1$$

$$\frac{\partial\Omega_2}{\partial y} = (2x_1 - x_3 - x_4)/\%1$$

$$\frac{\partial\Omega_3}{\partial y} = (-x_1 + x_2)/\%1$$

$$\frac{\partial\Omega_4}{\partial y} = (-x_1 + x_2)/\%1$$

$$\frac{\partial\Omega_4}{\partial y} = (-x_1 + x_2)/\%1$$

$$\frac{\partial\Omega_4}{\partial y} = (2x_1y_2 - x_2y_1) - (x_1y_3 - x_3y_1) + (x_4y_1 - x_1y_4) + (x_2y_3 - x_3y_2) + (x_2y_4 - x_4y_2)$$
(3.3.128)

For the point II with local coordinates (-1,0), (3.3.126) simplifies to:

$$\frac{\partial \Omega_1}{\partial x} = (y_2 - y_3)/\%1$$

$$\frac{\partial \Omega_2}{\partial x} = (-y_1 + 2y_3 - y_4)/\%1$$

$$\frac{\partial \Omega_3}{\partial x} = (y_1 - 2y_2 + y_4)/\%1$$

$$\frac{\partial \Omega_4}{\partial x} = (y_2 - y_3)/\%1$$

$$\frac{\partial \Omega_1}{\partial y} = (-x_2 + x_3)/\%1$$

$$\frac{\partial \Omega_2}{\partial y} = (x_1 - 2x_3 + x_4)/\%1$$

$$\frac{\partial \Omega_3}{\partial y} = (-x_1 + 2x_2 - x_4)/\%1$$

$$\frac{\partial \Omega_4}{\partial y} = (-x_2 + x_3)/\%1$$

$$\%1 = (x_1y_2 - x_2y_1) - (x_1y_3 - x_3y_1) + 2(x_2y_3 - x_3y_2) - (x_2y_4 - x_4y_2) + (x_3y_4 - x_4y_3)$$
(3.3.129)

For the point *III* with local coordinates (0,-1), (3.3.126) simplifies to:

$$\frac{\partial \Omega_1}{\partial x} = (y_3 - y_4)/\%1$$

$$\frac{\partial \Omega_2}{\partial x} = (y_3 - y_4)/\%1$$

$$\frac{\partial \Omega_3}{\partial x} = (-y_1 - y_2 + 2y_4)/\%1$$

$$\frac{\partial \Omega_4}{\partial x} = (y_1 + y_2 - 2y_3)/\%1$$

$$\frac{\partial \Omega_1}{\partial y} = (-x_3 + x_4)/\%1$$

$$\frac{\partial \Omega_2}{\partial y} = (-x_3 + x_4)/\%1$$

$$\frac{\partial \Omega_3}{\partial y} = (x_1 + x_2 - 2x_4)/\%1$$

$$\frac{\partial \Omega_4}{\partial y} = (-x_1 - x_2 + 2x_3)/\%1$$

$$\%1 = (x_1y_3 - x_3y_1) + (x_4y_1 - x_1y_4) + (x_2y_3 - x_3y_2) - (x_2y_4 - x_4y_2) + 2(x_3y_4 - x_4y_3)$$
(3.3.130)

For the point IV with local coordinates (1,0), (3.3.126) simplifies to:

$$\frac{\partial\Omega_1}{\partial x} = (y_2 + y_3 - 2y_4)/\%1$$

$$\frac{\partial\Omega_2}{\partial x} = (-y_1 + y_4)/\%1$$

$$\frac{\partial\Omega_3}{\partial x} = (-y_1 + y_4)/\%1$$

$$\frac{\partial\Omega_4}{\partial x} = (2y_1 - y_2 - y_3)/\%1$$

$$\frac{\partial\Omega_1}{\partial y} = (-x_2 - x_3 + 2x_4)/\%1$$

$$\frac{\partial\Omega_2}{\partial y} = (x_1 - x_4)/\%1$$

$$\frac{\partial\Omega_3}{\partial y} = (-2x_1 + x_2 + x_3)/\%1$$

$$\%1 = (x_1y_2 - x_2y_1) + (x_1y_3 - x_3y_1) + 2(x_4y_1 - x_1y_4) + (x_2y_4 - x_4y_2) + (x_3y_4 - x_4y_3)$$
(3.3.131)

The scheme as defined by (3.3.125) and (3.3.124) is not monotonic. This is due to the central differentiation scheme and due to the 9-point stencil which arises if the scheme is applied to a structured grid. To achieve monotonicity the scheme must be modified as follows:

- The fluxes across the inner-element subdomain boundaries are be evaluated by one-point integration at the element edges (points I, II, III and IV).
- Advective fluxes are be evaluated by upwind differentiation.
- Cross diffusion terms must be eliminated. These terms express the influence of nodal concentrations e.g. at the nodes 3 and 4 on the flux between the nodes 1 and 2, and cause oscillations near discontinuities.

Note that the monotonic scheme is identical to the monotonic integrated FDM approach, when applied to a structured grid.

#### 3.3.8.9 Mass Lumping

The structure of the mass matrix  $\underline{M}$  has been identified as a significant factor causing instabilities in FEM calculations. A diagonal matrix has been found to stabilize the scheme. In structural mechanics the physical interpretation of this mass lumping may be explained by Fig. 3.37: instead of a continuous mass distribution the mass is concentrated at the discretization nodes.

To achieve a diagonal mass matrix, at least three approaches are possible:



**Bilinear Interpolation** 

**Mass-Lumping** 

Figure 3.37: Physical interpretation of mass lumping.

- The FECV approach as described above divides the element into definite subdomains. This is the most physical development of a diagonal matrix.
- The mass matrix can be calculated by the standard FEM and then modified by summating all entries in a row.

$$m_{i,i}^{lump} = \sum_{k=1}^{n_N} m_{i,k}$$
(3.3.132)

• An alternative approach for diagonalization is to preserve the relation between the diagonal entries:

$$M_{diag} = \sum_{k=1}^{n_N} m_{k,k}$$

$$M_{tot} = \sum_{k=1}^{n_N} \sum_{i=1}^{n_N} m_{i,k}$$

$$m_{i,i}^{lump} = m_{i,i} \frac{M_{tot}}{M_{diag}}$$
(3.3.133)

#### 3.3.8.10 Flux-Corrected Transport

The Flux-Corrected Transport algorithm described for Finite Differences has been applied to Finite Elements by PARROTT & CHRISTIE [1986]. As low order and high order schemes can differ in the mass matrix a direct comparison of element contributions to a node is not possible. Extending an approach of LÖHNER ET AL. [1987] the high order method has to be reformulated:

$$\underline{\underline{M}}_{h} \frac{\partial \underline{\hat{c}}_{h}}{\partial t} = \underline{\underline{M}}_{h} \underline{\hat{r}} - \underline{\underline{A}}_{h} \underline{\hat{c}}_{h}$$

$$\Rightarrow \underline{\underline{M}}_{l} \frac{\partial \underline{\hat{c}}_{h}}{\partial t} = \underline{\underline{M}}_{h} \underline{\hat{r}} - \underline{\underline{A}}_{h} \underline{\hat{c}}_{h} + \left(\underline{\underline{M}}_{l} - \underline{\underline{M}}_{h}\right) \frac{\partial \underline{\hat{c}}_{h}}{\partial t} = \underline{\underline{HEC}}$$
(3.3.134)

and

$$\underline{\underline{M}}_{l}\frac{\partial \underline{\hat{c}}_{l}}{\partial t} = \underline{\underline{M}}_{l}\underline{\hat{r}} - \underline{\underline{A}}_{l}\underline{\hat{c}}_{l} = \underline{LEC}$$
(3.3.135)

Here  $\underline{\underline{M}}$  denotes the mass matrix,  $\underline{\underline{A}}$  is the mobility matrix and the subscripts h and l indicate the high order and low order scheme, respectively. <u>*HEC*</u> represents the high order element contribution vector to the nodes and <u>*LEC*</u> the low order element contribution vector. After solving the time step by both methods an antidiffusive element contribution vector can be calculated:

$$\underline{AEC} = \underline{HEC} - \underline{LEC}$$

$$= \left(\underline{M}_{h} - \underline{M}_{l}\right) \hat{\underline{r}} - \underline{A}_{h} \hat{\underline{c}}_{h} + \underline{A}_{l} \hat{\underline{c}}_{l} + \left(\underline{M}_{l} - \underline{M}_{h}\right) \frac{\partial \hat{\underline{c}}_{h}}{\partial t}$$
(3.3.136)

This antidiffusive element contribution vector has to be limited to preserve monotonicity by an element specific factor  $C_{el}$ :

$$\underline{AEC}^c = C_{el}\underline{AEC}, 0 \le C_{el} \le 1 \tag{3.3.137}$$

Summating  $\underline{AEC}^c$  over all elements with a common node leads to the correction of the low order solution:

$$\Delta c^i = \sum_{el} \underline{AEC}^c_i \tag{3.3.138}$$

$$\hat{c}_{fct}^{i} = c_{l}^{i} + \frac{\Delta t}{V_{Patch}^{i}} \Delta c^{i}$$
(3.3.139)

The limiting procedure consists of the following four steps:

#### Summating all positive/negative AEC's at a node

$$P_{i}^{+} = \sum_{el} max \left(0, AEC_{i}^{el}\right)$$

$$P_{i}^{-} = \sum_{el} min \left(0, AEC_{i}^{el}\right)$$
(3.3.140)

#### Definition of the maximum/minimum allowable AEC's at a node

$$Q_{i}^{+} = \frac{V_{i}^{Patch}}{\Delta t} \left( c_{i}^{max} - c_{i}^{l} \right)$$

$$Q_{i}^{-} = \frac{V_{i}^{Patch}}{\Delta t} \left( c_{i}^{min} - c_{i}^{l} \right)$$
(3.3.141)

 $c_i^{max}$  is the maximum concentration in the low order solution and in the last time step at any node sharing an element with the node of interest *i*.  $c_i^{min}$  is defined in the same manner as the minimum concentration.

# Calculating the ratio of $Q_i^\pm$ to $P_i^\pm$

$$\begin{aligned} R_{i}^{+} &= \min\left(1, \frac{Q_{i}^{+}}{P_{i}^{+}}\right) if P_{i}^{+} \neq 0 \\ &= 0 if P_{i}^{+} = 0 \\ R_{i}^{-} &= \min\left(1, \frac{Q_{i}^{-}}{P_{i}^{-}}\right) if P_{i}^{-} \neq 0 \\ &= 0 if P_{i}^{-} = 0 \end{aligned}$$
(3.3.142)

**Defining**  $C_{el}$ 

$$C_{el} = \min_{nodes_{el}} \begin{pmatrix} R_i^+ & if & AEC_i^{el} > 0\\ R_i^- & if & AEC_i^{el} < 0 \end{pmatrix}$$
(3.3.143)

# 3.4 Boundary Conditions

# 3.4.1 Fixed Concentrations (Dirichlet-B.C.)

In principle there are two ways of including fixed concentrations as boundary conditions. Assuming that the discretization scheme leads to a system of equations of the type (3.4.144):

$$\underline{M}\,\underline{c} = \underline{b} \tag{3.4.144}$$

then the matrix  $\underline{M}$  may be changed so that the line of the known concentration  $c_i$  is blanked out with the exception of the entry  $M_{i,i}$  which is set to unity. Additionally, the load vector  $\underline{b}$  is changed in entry  $b_i$  to the fixed concentration. In this case the order of the system of equations remains the same. If the matrix was symmetric before introducing the boundary condition, it subsequently becomes unsymmetric.

An alternative way is to delete the row i in  $\underline{M}$ ,  $\underline{c}$  and  $\underline{b}$ . The i'th column of  $\underline{M}$  has to be multiplied by the known concentration  $c_i$  and subtracted from  $\underline{b}$ . The transformed system of equations is now of one order less than the original system. Possible symmetry is preserved.

### 3.4.2 Fixed Mass Fluxes

#### 3.4.2.1 FEM with Weak Formulation of Diffusive Mass Fluxes

In this case advective mass fluxes out of the domain are already implemented in the formulation. Diffusive mass fluxes at outflow nodes are not implemented. In most cases advection dominates over diffusion, and hence the error is negligible. Furthermore, it is not clear whether the spatial derivatives are continuous over the boundary of the domain. This may differ from the physical type of boundary.

For inflow boundaries the total mass flux into the domain at the inflow node has to be added to the reactive source/sink term on the right-hand side of the system of equations. Along the main diagonal of the matrix on the right-hand side the water flux has to be added.

#### 3.4.2.2 FEM with Weak Formulation of Total Mass Fluxes and FDM Formulation

These schemes require explicit definitions of all mass fluxes across the boundary of the domain to be defined. At inflow nodes the total mass flux has to be added to the right-hand side of the system of equations. At outflow nodes the water fluxes have to be subtracted from the main diagonal of the matrix on the right-hand side. As in the previous case, diffusive mass fluxes across outflow boundaries are not considered. Additional terms may be added if desired.

# 3.5 FDM versus FEM - A Brief Comparison

#### **3.5.1 FEM expressed in terms of FDM**

Although the two approaches presented in this paper seem to be slightly different, they can be compared under the assumption of a structured, rectangular grid with regular spacing and constant coefficients. Evaluating the matrices of one node in the domain for FEM (Standard GALERKIN) and comparing it to FDM (central differentiation) leads to the following results:

- The advective FEM fluxes connecting one node with another are identical to the sum of three parallel FDM fluxes with the weightings 1/6 2/3 1/6.
- The same holds for the diffusive fluxes resulting from the diagonal entries  $D_{xx}$  and  $D_{yy}$  in the dispersion tensor. The terms for cross-diffusion are identical in FEM and FDM if 9-point differentiation is used in FDM.
- The FEM mass matrix is the sum of three parallel FDM mass matrices per spatial direction. The weightings are 1/6 2/3 1/6 per spatial direction.
- Mass lumping of FEM leads to a mass matrix identical to FDM, in which the mass fluxes are still identical to FEM.

- The truncation error terms evaluated by TAYLOR expansion are almost identical up to third order terms (see 3.5.145-3.5.147). Hence the correction terms in the TAYLOR-GALERKIN and LAX-WENDROFF schemes are identical.
- FDM upwinding and inconsistent PETROV-GALERKIN are not equivalent in the framework described above: upwind differentiation in FDM leads to artificial diffusion with a diagonal scaled diffusion tensor whereas the artificial diffusion introduced by the inconsistent PETROV-GALERKIN method is a dense tensor. If the upwind coefficients for the inconsistent PETROV-GALERKIN method are chosen properly, artificial diffusion can be restricted to longitudinal diffusion. For upwind differentiation in FDM this is only possible for a streamline-oriented grid. SUPG is not comparable to FDM since the mass matrix is changed.

Fig. 3.38 illustrates these results. Nodes are marked by circles, FDM cells have solid boundaries and FEM elements have dashed boundaries. FDM fluxes are illustrated by arrows. Weighting of FDM fluxes and mass matrix entries in FEM are illustrated by colour density.

#### **3.5.2** Truncation Error Analysis

 $\mathbf{O}$ 

The following truncation errors are for purely advective transport in two dimensions.

Truncation Error of Integrated Finite Differences:

$$\frac{\partial c}{\partial t} + v_x \frac{\partial c}{\partial x} + v_y \frac{\partial c}{\partial y} + \frac{\Delta t}{2} \frac{\partial^2 c}{\partial t^2} + \Theta \Delta t v_x \frac{\partial^2 c}{\partial x \partial t} + \Theta \Delta t v_y \frac{\partial^2 c}{\partial y \partial t} + \frac{\Delta t^2}{6} \frac{\partial^3 c}{\partial t^3} + \frac{\Delta x^2}{6} v_x \frac{\partial^3 c}{\partial x^3} + \frac{\Delta y^2}{6} v_y \frac{\partial^3 c}{\partial y^3} + \Theta \frac{\Delta t^2}{2} v_x \frac{\partial^3 c}{\partial x \partial t^2} + \Theta \frac{\Delta t^2}{2} v_y \frac{\partial^3 c}{\partial y \partial t^2} + H.O.T.$$
(3.5.145)

#### Truncation Error of Standard Finite Elements:

$$\frac{\partial c}{\partial t} + v_x \frac{\partial c}{\partial x} + v_y \frac{\partial c}{\partial y} 
+ \frac{\Delta t}{2} \frac{\partial^2 c}{\partial t^2} + \Theta \Delta t v_x \frac{\partial^2 c}{\partial x \partial t} + \Theta \Delta t v_y \frac{\partial^2 c}{\partial y \partial t} 
+ \frac{\Delta t^2}{6} \frac{\partial^3 c}{\partial t^3} + \frac{\Delta x^2}{6} v_x \frac{\partial^3 c}{\partial x^3} + \frac{\Delta y^2}{6} v_y \frac{\partial^3 c}{\partial y^3} + \Theta \frac{\Delta t^2}{2} v_x \frac{\partial^3 c}{\partial x \partial t^2} + \Theta \frac{\Delta t^2}{2} v_y \frac{\partial^3 c}{\partial y \partial t^2} 
+ \frac{\Delta x^2}{6} v_y \frac{\partial^3 c}{\partial x^2 \partial y} + \frac{\Delta y^2}{6} v_x \frac{\partial^3 c}{\partial x \partial y^2} + \frac{\Delta x^2}{6} \frac{\partial^3 c}{\partial x^2 \partial t} + \frac{\Delta y^2}{6} \frac{\partial^3 c}{\partial y^2 \partial t} + H.O.T.$$
(3.5.146)

0

0



Figure 3.38: Comparison of FDM using central differentiation and standard GALERKIN FEM.

Truncation Error of Finite Elements + Mass Lumping:

$$\frac{\partial c}{\partial t} + v_x \frac{\partial c}{\partial x} + v_y \frac{\partial c}{\partial y} 
+ \frac{\Delta t}{2} \frac{\partial^2 c}{\partial t^2} + \Theta \Delta t v_x \frac{\partial^2 c}{\partial x \partial t} + \Theta \Delta t v_y \frac{\partial^2 c}{\partial y \partial t} 
+ \frac{\Delta t^2}{6} \frac{\partial^3 c}{\partial t^3} + \frac{\Delta x^2}{6} v_x \frac{\partial^3 c}{\partial x^3} + \frac{\Delta y^2}{6} v_y \frac{\partial^3 c}{\partial y^3} + \Theta \frac{\Delta t^2}{2} v_x \frac{\partial^3 c}{\partial x \partial t^2} + \Theta \frac{\Delta t^2}{2} v_y \frac{\partial^3 c}{\partial y \partial t^2} 
+ \frac{\Delta x^2}{6} v_y \frac{\partial^3 c}{\partial x^2 \partial y} + \frac{\Delta y^2}{6} v_x \frac{\partial^3 c}{\partial x \partial y^2} + H.O.T.$$
(3.5.147)

#### 3.5.3 Grids

The main advantage of FEM over FDM is the suitability for unstructured grids, thus providing the opportunity to simulate complex geometries or to refine the grid locally. Unfortunately, however, stabilization of transport calculations is more complicated with unstructured grids than with structured ones.

A general Finite Volume approach (FVM) may also be suitable for unstructured grids. The main problem in this class of discretization methods lies in the approximation of cross-diffusion terms.

The optimal grid in a multidimensional domain both for FEM and FDM is oriented in the direction of streamlines. For streamline-oriented grids, advection occurs as a 1-D problem. Additionally, the dispersion tensor is diagonally scaled. For FDM this reduces the stencil to 5 points in 2-D and to 7 points in 3-D.

#### 3.5.4 Stability Considerations

Integrated Finite Differences are easier to stabilize than Finite Elements. A basic assumption of FEM is  $C_0$  continuity. Unfortunately, the true distribution of concentration can be discontinuous at the scale of discretization due to heterogeneity, reactions or local sources. In these situations FEM yields oscillatory results.

These oscillations can easily be explained within the framework of Fig. 3.38. The advective FDM flux from one cell to another is only dependent on the concentrations in these two cells. At least full upwinding guarantees monotonicity under this condition. The advective FEM flux from one node to another is dependent on the concentrations at these two nodes and on the concentrations at all other nodes belonging to elements shared by both nodes of interest. This influence of additional nodes can lead to oscillations if concentration jumps exist.

Note that this type of relationship also occurs in the cross-diffusion terms of FDM. These terms do not occur only on streamline-oriented FDM grids.

# **3.6 Benchmark Tests for Advective-Dispersive Transport**

#### **1-D Point Source Test** 3.6.1

A classical one-dimensional benchmark test for advective-dispersive transport is the HEAVISIDE problem, in which the initial concentration is uniform (e.g. 0.0) and the inflow concentration at the inflow boundary of the domain is constant but different to the initial concentration (e.g. 1.0). Particularly for high PECLET numbers this test gives a good indication as to whether a numerical scheme is stable near a moving discontinuity. The analytical solution to this problem is given by [48]. (3.6.148) is valid for a non-retarded compound.

$$c(x,t) = \frac{c_{in}}{2} \operatorname{erfc}\left(\frac{x - v_e t}{2\sqrt{(\alpha v_e + D_m)t}}\right)$$
(3.6.148)

The benchmark test was extended to test the behaviour of the numerical schemes near stationary discontinuities, which may occur due to point sources. Therefore the initial concentration over the entire domain was set to zero. The inflow concentration was set to zero as well. At an interior point of the domain the concentration was maintained at unity over the entire simulation period. For all nodes downstream of this point source the problem is identical to the HEAVISIDE problem. Additionally, the behaviour of the numerical scheme is also tested at the nodes upstream of the point-source.

For the nodes upstream of the point-source the concentration profiles converge to the steady-state solution (3.6.149):

$$c(x) = \frac{1 - e^{v_e x/D}}{1 - e^{v_e x_s/D}}$$
(3.6.149)

in which  $x_s$  is the distance of the point source from the inlet. The chosen parameters for the test runs are summarized in Table 3.1. For the tested FEM schemes the weak formulation of total mass

Table 3.1: Parameters for the one-dimensional point source test.		
Flow and transport parameters		
$K = 10^{-3} m/s$ $\phi_e = 0.1$	$\alpha = .01 \mathrm{m}$	$D_m = 10^{-9} \text{ m}^2/\text{s}$
Geometric parameters		
Length of the domain: 100m	$x_s = 10 \mathrm{m}$	$\Delta x = 1$ m
Boundary conditions for the flow field		
$h_{inflow}$ - $h_{outflow} = 1.0m$		
Discretization in time		
$\Delta t = 5.000 \mathrm{s}$ for FEM models	adaptive $\Delta$	t for FDM models
Resulting dimensionless numbers		
$Pe = 100 \qquad Cr_{FEM} = 0.5$	$Cr_{FDM}$ var	riable

----C .1 1 . 1 .

adopted. All tested FDM schemes include the slope limiter approach in a semidiscrete formulation. Linearization and integration in time was carried out using the DAES-solver DASPK (see Sections 4.1 and 5.3).

Fig. 3.39-3.48 show length profiles of concentration obtained for different numerical schemes. The profiles are shown for the times 20,000s, 40,000s, 60,000s, 80,000s and 100,000s after the start of simulation.



Figure 3.39: 1-D point source test, standard GALERKIN.

Fig. 3.39 shows length profiles given by the Standard GALERKIN method, as described in Section 3.3.8.1. At the moving front the scheme leads to oscillations at the upstream tail of the front whereas no oscillations occur at the downstream head of the front. Note that for the given one-dimensional problem without source-sink terms the CRANK-NICOLSON time integration is equivalent to explicit time integration using second order TAYLOR-GALERKIN stabilization. Since the resulting mobility matrix is identical to FDM using central differentiation, the stability of the scheme can be discussed in the context of TVD stability as introduced in Section 3.2.4.2.2.

For the stated model problem the CRANK-NICOLSON standard GALERKIN scheme is therefore equivalent to an extended GODUNOV scheme where the innercell concentration distribution has a slope s of  $s_{lin}^{dwn}$ , as obtained by linear interpolation to the downstream node. For a regular grid this scheme leads to oscillations for any curvature  $\theta$  (as defined in 3.2.28) smaller than 0.5 (see Fig. 3.9). Note that at the downstream head of the moving front  $\theta$  exceeds 1.0 because the upstream slope is larger than the downstream slope. The very small value of  $\theta$  at the upstream tail of the moving front causes oscillations to occur.

However, the instabilities upstream of the stationary discontinuity are much more significant than the instabilities near the moving front. These instabilities can again be explained in the context of Fig. 3.9

since the true solution shows a concentration distribution with a small slope further upstream of the discontinuity and a sudden rise in the slope directly in front of the point source.



Figure 3.40: 1-D point source test, TAYLOR-GALERKIN.

Fig. 3.40 shows length profiles obtained from the TAYLOR-GALERKIN scheme explained in Section 3.3.8.3. The scheme leads to no significant improvement. Oscillations at the upstream tail of the moving front are slightly damped. However, small oscillations occur at the downstream head of the moving front. This is caused by the third-order correction terms introduced into the scheme. The instabilities upstream of the point source are identical to the standard GALERKIN scheme.

Fig. 3.41 shows length profiles obtained from the SUPG scheme explained in Section 3.3.8.5. Using an upwind coefficient optimized for steady-state problems (3.3.102) supresses the instabilities upstream of the point source. However, at the usptream tail as well as at the downstream head of the moving front spurious oscillations occur. Allthough these oscillations do not increase with time they may be inacceptable in the context of reactive transport. The scheme shows no significant artificial diffusion. This is due to the consistent formulation of upwinding in the SUPG method.

Fig. 3.42 shows length profiles obtained from the inconsistent PETROV-GALERKIN scheme explained in Section 3.3.8.4 using the upwind coefficient of NOORISHAD ET AL. (3.3.107). The results are identical to the standard GALERKIN solution with artificial diffusion as explained in Section 3.3.8.2. The effect of artificial diffusion is clearly indicated by excessive smearing at the moving front. Near the moving front no oscillations occur. However, artificial diffusion produced by the scheme is not sufficient to stabilize the solution upstream of the stationary discontinuity.

Note that the upwind coefficient for the scheme decreases with decreasing COURANT number. Since the stationary discontinuity leads to a quasi-steady-state problem, the upwind coefficient for this problem should be independent of the time discretization. In fact the scheme is developed from amplifi-



Figure 3.41: 1-D point source test, Streamline Upwind PETROV-GALERKIN.



Figure 3.42: 1-D point source test; inconsistent PETROV-GALERKIN scheme (Cr\*Pe=2).

cation matrix analysis. The introduction of boundary conditions such as the point-source changes the matrix to be analyzed. This was not considered in [49].



Figure 3.43: 1-D point source test, inconsistent PETROV-GALERKIN scheme  $\alpha = coth(Pe/2) - 2/Pe$ .

Fig. 3.43 shows length profiles obtained from the inconsistent PETROV-GALERKIN scheme explained in Section 3.3.8.4 using the upwind coefficient optimized for steady-state problems (3.3.102). Choosing this upwind coefficient leads to stabilization upstream of the stationary discontinuity. However, the artificial diffusion produced by the scheme smears the moving front to an unacceptable extent. Note that FDM schemes using simple upwind differentiation would yield equivalent length profiles.

Fig. 3.44 shows length profiles obtained from the Flux-Corrected-Transport scheme for FEM as explained in Section 3.3.8.10. The inconsistent PETROV-GALERKIN method using the upwind coefficient optimized for steady-state problems was adopted as the low-order method, whereas the TAYLOR-GALERKIN scheme was applied as the high-order method. The FCT solution shows no oscillations and minimal artificial diffusion. Note that similiar results would be obtained from the FCT scheme based on FDM.

Figures 3.45-3.48 illustrate length profiles for different slope limiter schemes. All of these are free of oscillations. However, the different schemes produce different amounts of artificial diffusion.

Fig. 3.45 shows the results for the *minmod* slope limiter. In the context of Fig. 3.10 this scheme reflects the lower limit of the second-order TVD region. Since the sharpness of the front increases with increasing slope, the *minmod* limiter introduces a remarkable amount of artificial diffusion. However, this artificial diffusion is still moderate compared to the artificial diffusion produced by full upwinding.



Figure 3.44: 1-D point source test; FEM Flux-Corrected Transport. High order scheme: TAYLOR-GALERKIN. Low order scheme: inconsistent PETROV-GALERKIN scheme.



Figure 3.45: 1-D point source test; *minmod* slope limiter.



Figure 3.46: 1-D point source test; HAEFNER's front limiter.

Fig. 3.46 shows the results for HAEFNER's front limiter. This scheme mainly follows the BEAM-WARMING line. This represents the upper limit of the second-order TVD region for a curvature  $\theta$  ranging from 1.0 to 2.0, and the lower limit of the second-order TVD region for curvature  $\theta$  ranging from 0.0 to 1.0. As a consequence the profiles are very sharp at the downstream head of the moving front and are smeared at the upstream tail of the moving front.



Figure 3.47: 1-D point source test; ROE's Superbee limiter.

Fig. 3.47 shows the results for ROE's *Superbee* limiter. This scheme generally follows the upper limit of the second-order TVD region. As a consequence, the shape of the front is very sharp both at the head and the tail of the moving front. In [33] test calculations are shown indicating over-sharpening of this method.

Note that the computational effort for the *Superbee* limiter was much higher than for the *minmod* limiter. This result only holds if implicit time integration is used. Similiar results were obtained by REICHERT [51] when comparing the *Superbee* limiter to VAN LEER's limiter. He explained this behaviour by the non-differentiable nature of the limiter function. This explanation cannot be valid when comparing the *Superbee* limiter to the *minmod* limiter since both limiters are piecewise linear. In the opinion of the author the smoothness of the solution is much more important for the performance of the scheme than the smoothness of the limiter function. The DAES solver is based on polynomial interpolation. For the tested model problem, time profiles of concentrations at nodes contain sharp steps. Therefore polynomial extrapolation yields a poor predictor for concentration development at "front nodes". The sharper the front, the smaller the time step has to be, in order to obtain the required accuracy. This is a general disadvantage of the method of lines approach.



Figure 3.48: 1-D point source test; VAN LEER's slope limiter.

Fig. 3.48 shows the results for VAN LEER's limiter. The sharpness of the solution lies between that of the *Superbee* and the *minmod* limiter. The shape of the front is as symmetric as in the latter two approaches.

With regard to all the methods tested, it may be concluded that all linear schemes suffer either from oscillatory behaviour, e.g. as in the case of the standard GALERKIN scheme or SUPG, or from excessive artificial diffusion, e.g. as in the case of the inconsistent PETROV-GALERKIN method. High-order accurate schemes which preserve monotonicity must be nonlinear. An easy-to-implement nonlinear scheme is the FCT method. Allthough this scheme doubles the computational effort it requires no further - possibly even more costly - linearization. As an alternative the slope limiter schemes may be used. For one-dimensional problems without source/sink terms these may be integrated explicitly. Implicit time integration as used in the present study increases the computational effort dramatically. This may be different in the case of nonlinear reactive transport, as the reactive terms cannot be integrated explicitly.

#### **3.6.2 2-D** Point Source Test with a Homogeneous Flow Field

In order to test the behaviour of the selected schemes for multidimensional problems the point source test was extended to two dimensions. Two situations of parallel flow field were tested: a situation in which the flow is parallel to the grid (see Figs. 3.49 and 3.50), and a situation in which it is diagonal to the grid (see Figs. 3.51-3.53). For the 2-D test a steady-state transport problem was chosen. The grid spacing was 1m both in the x and y direction. The longitudinal dispersivity was 0.01m and the transverse dispersivity 0.001m.

Since the oscillatory behaviour of the standard GALERKIN method, the TAYLOR-GALERKIN method and the SUPG method has already been demonstrated in the 1-D point-source test, the two-dimensional test was limited for FEM to the inconsistent PETROV-GALERKIN scheme in two versions and the FCT scheme.



Figure 3.49: 2-D point source test for a flow field parallel to the grid. Inconsistent PETROV-GALERKIN method for bilinear FEM discretization.

Fig. 3.49 shows the concentration distribution for the 2-D point source test with flow parallel to the grid using the inconsistent PETROV-GALERKIN method for bilinear FEM discretization as explained in Section 3.3.8.4. In contrast to the one-dimensional test case, the scheme yields an oscillatory solution for multidimensional problems.

This may be explained in the context of Fig. 3.38. The mobility matrix for bilinear FEM includes flux terms from a node to a neighbouring node which are dependent on parallel nodes. For the stated model problem this leads to a positive flux from a node parallel to the point source to its downstream neighbour. Since there is no mass flux towards this parallel node, mass balance can only be achieved by a negative concentration. The minimum concentration obtained by the scheme was -0.265 for a fixed point-source concentration of 1.0.

Note that this is a direct result of 9-point differentiation. Mass lumping or application of the SUPG method cannot overcome this problem as a mass matrix is notconsidered in steady-state problem.



Figure 3.50: 2-D point source test for flow field parallel to grid. Inconsistent PETROV-GALERKIN method for 5-point Finite Element Control Volume discretization.

Fig. 3.50 shows the concentration distribution for the 2-D point-source test with flow parallel to the grid using the inconsistent PETROV-GALERKIN method for 5-point FECV discretization as explained in Section 3.3.8.8. The evaluation of advective mass fluxes at element edges avoids oscillations. The minimum concentration obtained by the scheme was  $-5.8 \cdot 10^{-30}$ , which is within the range of the computer cut-off error.

Note that the FECV approach is identical to integrated FDM when rectangular grids are used. The comparison of Figs. 3.49 and 3.50 indicates, as stated in Section 3.5.4, that Finite Differences and Finite Volume methods are easier to stabilize than Finite Element methods. However, they may be

problematic if the grid is not oriented in the direction of streamlines.



Figure 3.51: 2-D point-source test a for flow field diagonal to the grid. Inconsistent PETROV-GALERKIN method for bilinear Finite Element discretization.

Fig. 3.51 shows the concentration distribution for the 2-D point-source test with flow diagonal to the grid using bilinear FEM discretization. As in the case of grid-parallel flow, oscillations occur. The minimum concentration obtained by the method was -0.097.

However, the plume caused by the point source is rather narrow. After initial spreading directly near the point source the maximum concentration in the plume decreases slowly along the pathline. This good approximation of transverse dispersivity is due to the 9-point differentiation included in the scheme.

Fig. 3.52 shows the concentration distribution for the 2-D point-source test with flow diagonal to the grid using 5-point FECV discretization. As in the case of the grid-parallel flow the scheme preserves monotonicity. The minimum concentration obtained by the method was  $-1.1 \cdot 10^{-10}$ . However, the method introduces excessive transverse diffusion. The maximum concentration in the plume decreases rapidly along the pathline.

This excessive transverse diffusion is due to the combined effect of upwinding and 5-point differentiation. Proper upwinding leads to artificial longitudinal diffusion which results in a dense diffusion tensor if the direction of advective transport is not aligned with the grid. In FEM with bilinear elements this dense tensor can be approximated properly owing to the underlying 9-point differentiation for advective transport. In the case of 5-point differentiation this is not possible. Only diagonal tensors can be approximated. Note that this is independent of the method used to approximate diffusive transport.



Figure 3.52: 2-D point-source test for a flow field diagonal to the grid. Inconsistent PETROV-GALERKIN method for 5-point FECV discretization.



Figure 3.53: 2-D point source-test for a flow field diagonal to the grid. FCT method, low-order method: inconsistent PETROV-GALERKIN method for 5-point FECV discretization, high-order method: Standard GALERKIN.

In order to combine monotonicity preservation of the 5-point FECV method with the good approximation of diagonal mass flux in bilinear FEM discretization, the FCT method was used. As the FCT method is restricted to transient problems the 2-D point-source test was modified to a transient test. In Fig. 3.53 the resulting concentration distribution is shown for 60 time steps after the start of the simulation. Since the grid-oriented COURANT number  $Cr_x = v_x \Delta t / \Delta x$  was 1.0, Fig. 3.53 represents the steady-state solution of the problem.

Inconsistent upwinding using 5-point FECV discretization was used in the low-order method, while the standard GALERKIN method was the high-order method. The overall scheme combines the advantages of the two sub-schemes. The minimum concentration obtained by the method was  $-7.7 \cdot 10^{-9}$ . The maximum concentration in the plume decreases slowly along the pathline.



Figure 3.54: 2-D point source-test for a flow field diagonal to the grid. *Minmod* slope limiter.

Figs. 3.54 + 3.55 show the results for the slope limiter techniques described in Section 3.2.4.2.2. As in the one-dimensional test case the scheme is free of oscillations. Again the ROE's *Superbee* limiter (see Fig. 3.55) leads to a sharper front than the *minmod* limiter. However, the computational effort was very high.

#### **3.6.3 Rotating Prism**

A classical test for multi-dimensional numerical schemes is the rotating-cone test [6, 9], in which a concentration peak of GAUSSIAN shape is moved in a rotating flow field. The results after one rotation are compared to analytical solutions. In the case of pure advective transport the concentration



Figure 3.55: 2-D point source-test for a flow field diagonal to the grid. Superbee slope limiter.



Figure 3.56: 2-D point-source test for a flow field diagonal to the grid. Finite Difference Flux-Corrected-Transport method, low-order method: full upwinding, high-order method: central differentiation.

distribution after one rotation must correspond with the initial condition. In [28] the test is modified by adopting a cylindrical concentration distribution as the initial condition. In the present study a hexahedral prism was used. The problem statement is illustrated by 3.57.



Figure 3.57: Rotating prism 2-D test; Problem statement.

The grid spacing was 1m both in the x and y directions with a discretization of 50 by 50 nodes. The rotational velocity was 1 rotation in  $10^5$ s. The longitudinal dispersivity  $\alpha_l$  was 0.01m, whereas the transverse dispersivity  $\alpha_t$  was 0.001m. The time discretization was taken to be 250s, so that the COURANT number does not exceed unity anywhere in the domain. In the initial state a block of 7 by 7 nodes was set to unity while all other nodes were set to zero. Figs. 3.58-3.64 show concentration distributions after one rotation (400 time steps) for different discretization schemes.

The test was carried out only for FEM discretization schemes. In order to minimize boundary effects the weak formulation of total mass flux was used. No mass flux was permitted across the boundary of the domain.

Figs. 3.58 and 3.59 show concentration distributions after one rotation for the standard GALERKIN and the TAYLOR-GALERKIN method, respectively. Standard GALERKIN discretization leads to dramatic oscillations. The TAYLOR-GALERKIN scheme is oscillatory as well but to a lower extent. These findings are in good agreement with the oscillations observed near the moving discontinuity in the 1-D point-source test.

Figs. 3.60 and 3.61 show the results with artificial diffusion according to the approach of NOOR-ISHAD ET AL. as well as the inconsistent PETROV-GALERKIN method with upwinding derived from the steady-state solution. Although both schemes exhibit excessive artificial diffusion they are unable to suppress oscillations. This is an effect of multi-dimensionality. In the one-dimensional test both



# **Standard-Galerkin Scheme**

Figure 3.58: Rotating prism 2-D test; Standard GALERKIN (CRANK-NICOLSON time integration).



Figure 3.59: Rotating prism 2-D test; TAYLOR-GALERKIN (CRANK-NICOLSON time integration).

schemes were free of oscillations near the moving discontinuity. As was shown in Section 3.5.1, FEM fluxes between two nodes are dependent on neighbouring nodes. The only way to balance these fluxes near discontinuities is to introduce over- and under-shooting concentrations. Streamline-oriented artificial diffusion is not able to smear this out completely.



Figure 3.60: Rotating prism 2-D test; artificial diffusion (CRANK-NICOLSON time integration).

The results for the SUPG method are shown in Fig. 3.62. Allthough the scheme is non-diffusive, as in the 1-D point-source test, it nevertheless introduces spurious oscillations. For the purpose of conservative transport these oscillations may be tolerable. In the case of reactive transport, however, they are not.

Fig. 3.63 shows the concentration distribution for the FECV approach using 5-point differentiation and steady-state upwinding. The results are almost free of oscillations. Remaining undershoots are a result of 9-point differentiation for diffusive fluxes.

For the tested linear methods the FECV approach is the only possible choice for the low-order method in the FCT algorithm. The reason for this is that the FCT method preserves monotonicity only provided the low-order method also preserves monotonicity. Fig. 3.64 shows the concentration distribution after one rotation for the FCT method using FECV as the low-order method and the TAYLOR-GALERKIN scheme as the high-order method. This scheme introduces only minimal artificial diffusion and no oscillations. The shape of the original prism is still discernable after one rotation.

As a concluding remark on the tested schemes, it may be stated that classical FEM schemes are not suitable for advection-dominated transport if oscillations cannot be tolerated. If spurious oscillations are acceptable the SUPG method is an efficient approach, introducing limited oscillations and no artificial diffusion. The FECV approach, which was the only monotonic scheme, should be seen as a Finite Volume technique. The FCT approach allows the combination of FECV with a high-order FE



Figure 3.61: Rotating prism 2-D test; inconsistent PETROV-GALERKIN (CRANK-NICOLSON time integration).



Figure 3.62: Rotating prism 2-D test; Streamline Upwind PETROV-GALERKIN (CRANK-NICOLSON time integration).


Figure 3.63: Rotating prism 2-D test; FECV with 5-point differentiation and steady-state upwinding (CRANK-NICOLSON time integration).



Figure 3.64: Rotating prism 2-D test; Flux-Corrected Transport, (CRANK-NICOLSON time integration).

method, thus leading to non-oscillatory high-order solutions. Unfortunately, however, the combination of FECV with the SUPG method is inpractical since the mass matrix is significantly changed in the SUPG method.

# **Chapter 4**

# **Calculation of Reactive Processes**

As explained in Chapter 2, the governing equations describing reactive processes can be:

- Systems of (nonlinear) algebraic equations (AES) if thermodynamic equilibrium is assumed locally,
- Systems of (nonlinear) ordinary differential equations (ODES) if reactions are controlled by kinetics, or
- Systems of (nonlinear) differential algebraic equations (DAES) if both types of reactions occur.

The solution of nonlinear DAES is the most general case and will be delat with here. The following requirements have to be fulfilled by an appropriate solution scheme:

- Nonlinearity requires stable linearization.
- Stiffness requires fully implicit integration in time.
- Accuracy requires a multistep approach to obtain an order of consistency exceeding one.
- For reasons of stability and efficiency, adaptivity in time discretization and choice of order is preferable.

These stringent requirements can only be fulfilled by schemes specially developed for DAES. If a loss of accuracy can be tolerated, decoupling of algebraic and differential equations will be efficient [41, 27]. In CONTRACT only the first strategy is adopted.

## 4.1 Coupled Solution of DAES by DASSL

In the following a brief introduction is given concerning the algorithms implemented in the DAES-solver DASSL [50]. A more detailed description of the underlying concepts can be found in [4].

DASSL solves DAES of the general form (4.1.1):

$$F\left(t, y, \frac{\partial y}{\partial t}\right) = 0$$

$$y(t_0) = y_0$$

$$\left. \frac{\partial y}{\partial t} \right|_{t_0} = y'_0$$
(4.1.1)

The solution strategy follows backward differentiation. In a simple first order approach the DAES given by (4.1.1) may be converted to (4.1.2):

$$F\left(t_{n+1}, y_{n+1}, \frac{y_{n+1} - y_n}{\Delta t_{n+1}}\right) = 0$$
(4.1.2)

This nonlinear system is then usually solved using some variant of NEWTON's method. (4.1.2) is the implicit EULER scheme. Instead of linear interpolation in time, DASSL uses *k*th order polynomial interpolation, where *k* ranges from 1 to 5. Dependent on the behaviour of the solution, a new choice of the order *k* and the stepsize  $\Delta t_{n+1}$  is done on every step.

DASSL employs a variable stepsize/variable order fixed leading coefficient implementation of backward differentiation formulae, based on a predictor-corrector algorithm. For a given order k and stepsize  $\Delta t_{n+1}$  an initial estimate of  $y_{n+1}$  and  $y'_{n+1}$  is evaluated by polynomial extrapolation of the last k + 1 solutions. The predictor polynomial fulfills (4.1.3):

$$\omega_{n+1}^P(t_{n-i}) = y_{n-i} \qquad i = 0, 1, \dots, k$$
(4.1.3)

and the initial estimate is evaluated by:

$$y_{n+1}^{(0)} = \omega_{n+1}^{P}(t_{n+1})$$

$$y_{n+1}^{(0)} = \omega_{n+1}^{P}(t_{n+1})$$
(4.1.4)

In general this approximation will not fulfill (4.1.1). The finally accepted solution is the solution to the corrector formula. This corrector formula is no longer a direct polynomial interpolation of the new timestep and the last k solutions, but a polynomial which interpolates the predictor polynomial at k equally spaced points before  $t_{n+1}$ :

$$\omega_{n+1}^{C}(t_{n+1}) = y_{n+1} 
\omega_{n+1}^{C}(t_{n+1} - i\Delta t_{n+1}) = \omega_{n+1}^{P}(t_{n+1} - i\Delta t_{n+1}) \quad 1 \le i \le k$$

$$F\left(t_{n+1}, \omega_{n+1}^{C}(t_{n+1}), \omega_{n+1}^{C}(t_{n+1})\right) = 0$$
(4.1.5)



Figure 4.1: Principle of the variable stepsize fixed leading coefficient backward differentiation approach. Upper figure: Construction of the predictor polynomial. Lower figure: Constraints on the corrector polynomial. Squares: Solutions of previous time steps, triangle (upwards): Initial estimate of new time step, triangle (downwards): Equally spaced points before  $t_{n+1}$ . Dots coincide with triangles (downwards) except for  $t_{n+1}$ .

The principle of the scheme is illustrated in Fig. 4.1. After some rearrangements it is evident that the corrector iteration must solve:

$$F\left(t_{n+1}, y_{n+1}, y_{n+1}^{(0)} - \frac{\alpha_s}{\Delta t_{n+1}} (y_{n+1} - y_{n+1}^{(0)})\right) = 0$$
(4.1.6)

for  $y_{n+1}$ , where  $\alpha_s$  is defined by:

$$\alpha_s = -\sum_{j=1}^k \frac{1}{j}$$
(4.1.7)

(4.1.6) may be rewritten as:

$$F(t, y, \alpha y + \beta) = 0 \tag{4.1.8}$$

in which  $\alpha = -\alpha_s / \Delta t_{n+1}$  and  $\beta = y_{n+1}^{(0)} - \alpha y_{n+1}^{(0)}$ . Provided the order and time step do not change,  $\alpha$  remains constant and  $\beta$  only has to be evaluated once per time step. (4.1.8) is solved by a modified NEWTON iteration given by:

$$y^{(m+1)} = y^{(m)} - cJ^{-1}F(t, y^{(m)}, \alpha y^{(m)} + \beta)$$
(4.1.9)

in which m is the iteration index,  $y^{(0)}$  is the initial estimate of (4.1.4), and c is a scalar correction factor which is applied if the stepsize or order has changed since the last update of the JACOBIAN J as defined by:

$$J = \alpha \frac{\partial F}{\partial y'} + \frac{\partial F}{\partial y}$$
(4.1.10)

The rate of convergence  $\rho$  is estimated by (4.1.11) whenever two or more corrector iterations have been applied.

$$\rho = \left(\frac{\|y^{(m+1)} - y^{(m)}\|}{y^{(1)} - y^{(0)}}\right)^{1/m}$$
(4.1.11)

The final convergence criterion is given by:

$$\frac{\rho}{1-\rho} \|y^{(m+1)} - y^{(m)}\| < 0.33 \tag{4.1.12}$$

If  $\rho > 0.9$  or m > 4, and the iteration has not yet converged, the JACOBIAN must be reevaluated and/or the stepsize to be reduced. See [4] for the selection strategy of the order of approximation. The norm used in (4.1.11) and (4.1.12) is a weighted root-mean-square norm:

$$\|y\| = \left(\frac{1}{N}\sum_{i=1}^{N} \left(\frac{y_i}{w_i}\right)\right)^{1/2}$$
(4.1.13)

in which  $w_i$  are *i*th component weightings, which are based on user-defined relative and absolute tolerances  $\varepsilon_{i,rel}$  and  $\varepsilon_{i,abs}$ :

$$w_i = \varepsilon_{i,rel} |y_i| + \varepsilon_{i,abs} \tag{4.1.14}$$

The original DASSL library solves the resulting linear equations by direct solution techniques in the LINPACK package. It requires either a full or banded JACOBIAN matrix. The new solver DASPK [7], which is based on the iterative GMRES, algorithm can handle a sparse matrix definition of the JACOBIAN.

Note that the DAES solver requires consistent initial conditions including time derivatives. The latter is trivial in the case of first-order ODES but it is not in nonlinear DAES. Furthermore, the performance of the solver increases with increasing time steps (the first time step can only be of first-order and is automatically set to a very small size,). Hence, solving frequently restarted small problems may take a longer time than solving a large problem only once. This is of particular relevance in the discussion of methods for the coupling of chemistry and transport.

## Chapter 5

## **Coupling of Chemistry and Transport**

## 5.1 Operator Split Approach

The basic idea of the operator split approach as introduced in general by YANENKO [71] is to split the coupled problem into a transport problem and a reactive problem, both of which are solved independently and sequentially (5.1.1):

$$c(t_{n+1}) = c(t_n) + \Delta c_{trans} + \Delta c_{chem}$$
(5.1.1)

This yields the following scheme:

1. Take  $c(t_n)$  as the initial condition and solve:

$$\tilde{c}_{n+1} = \int_{t_n}^{t_{n+1}} transp. without chem. dt$$

2. Take  $\tilde{c}_{n+1}$  as the initial condition and solve:

$$c(t_{n+1}) = \int_{t_n}^{t_{n+1}} chem. without transp. dt$$

3. Goto next time step.

One linear PDE per mobile compound has to be solved in the transport step and one nonlinear DAES per node or cell in the chemistry step.

It should be mentioned that certain variations of the method exist, e.g. the three-step approach of STRANG [61] in which a transport step over the first half time step is followed by a chemistry step over the entire time step and a second transport step over the second half time step.

The operator split approach has some obvious advantages. It is easy to implement, computational costs are low, and the transport scheme can be optimized independently of the scheme for reactive processes.

The main problem of the approach lies in the introduction of an unknown coupling error. Allthough the modelled processes interact and occur in parallel, they are in fact treated independently in sequence. By choosing a sufficiently small time step, instabilities may be avoided. To the knowledge of the author corresponding error estimators exist only for simplified situations such as linear decay or single MICHAELIS-MENTEN kinetics [37, 46].

The operator-split approach is implemented in CONTRACT-3.

### 5.2 Iterative Two-Step Approach

Introducing iteration into the operator split approach can limit the coupling error of the scheme below a definite level. KINZELBACH ET AL. [39] applied a reactive sink-source term in the transport step, which is iteratively updated by the chemistry step. As for the operator split approach, the intermediate concentration  $\tilde{c}$  was taken as the initial condition for the chemistry step.

CIRPKA & HELMIG [14] modified this method so that the concentration at the previous time step is applied as the initial condition in both half-steps. This requires the definition of an explicit transport rate in the chemistry step. The basic principle may be explained by (5.2.2):

$$c_i(t_{n+1}) = \int_{t_n}^{t_{n+1}} \tau_i + r_i \, dt$$
(5.2.2)

where  $\tau_i$  is the transport rate for compound *i* at the node of interest and  $r_i$  is the reactive source-sink term. In the transport step  $\tau_i$  is calculated implicitly and  $r_i$  explicitly, whereas in the chemistry step,  $\tau_i$  is an explicit zero-order term and  $r_i$  is calculated implicitly. This leads to the following scheme:

1. For initialization of the new time step take the old reactive sink-source term as the initial estimate:

$$r_{i,n+1}^{(0)} = r_{i,n}$$

2. Take  $c_i(t_n)$  as the initial condition for the transport step:

$$c_{i,n+1}^{trans,(\nu)} = \int_{t_n}^{t_{n+1}} trans - r_{i,n+1}^{(\nu-1)} dt$$

3. Calculate an explicit transport rate for iteration step  $\nu$ :

$$\tau_{i,n+1}^{(\nu)} = \frac{c_{i,n+1}^{trans,(\nu)} - c_i(t_n)}{t_{n+1} - t_n} + r_{i,n+1}^{(\nu-1)}$$

4. Take  $c(t_n)$  as the initial condition for the chemistry step:

$$c_{i,n+1}^{chem,(\nu)} = \int_{t_n}^{t_{n+1}} chem + \tau_{i,n+1}^{(\nu)}$$

5. Calculate an explicit reactive sink-source term for iteration step  $\nu$ :

$$r_{i,n+1}^{(\nu)} = \frac{c_{i,n+1}^{chem,(\nu)} - c_i(t_n)}{t_{n+1} - t_n} - \tau_{i,n+1}^{(\nu)}$$

6. Check convergence:

$$\|c_{i,n+1}^{chem,(\nu)} - c_{i,n+1}^{trans,(\nu)}\| < \varepsilon_i$$
?

7. Either return to the transport step with  $\nu = \nu + 1$  or advance to the next time step.

This scheme is implemented in CONTRACT-FEM.

As in the operator split approach, one linear PDE per each mobile compound has to be solved in every transport step, and one nonlinear DAES per each node or cell in every chemistry step.

The main advantage over the operator-split method is the control of the coupling error. This advantage is at the expense of the multiple evaluation of both half-steps, leading to higher computational effort. The two methods can still be optimized almost independently of each other. As the implementation is fairly simple, almost every EULERIAN transport model can be extended to reactive multi-component transport.

A problem of the approach is that convergence of the scheme is not guaranteed for an arbitrary choice of time step. Besides the CFL condition, which is stated for many conservative transport schemes, a limitation of the stepsize arises from the convergence behaviour of coupling. In order to achieve efficiency this should be done in an adaptive way. A possible criterion for reducing the stepsize could be a specified maximum number of iterations or the rate of convergence. At present CONTRACT-FEM includes no adaptivity in time discretization.

Note that the iterative two-step method includes two linearizations, one for coupling and one implemented in the chemistry scheme. If a nonlinear scheme is applied in the transport step even a third linearization is necessary. Under certain circumstances this can be less efficient than a direct coupling scheme with consistent linearization of the entire set of equations.

## 5.3 Direct Coupling

In the direct coupling approach the PDE for transport and the DAES for chemistry are solved simultaneously. MACQUARRIE ET AL.[44] acieved this by adding a nonlinear first-order term for chemistry to the transport equation, which was then solved by the FEM technique. Linearization was performed by PICARD iteration. In a three-dimensional application [22] they simplified the approach by explicit treatment of the reaction terms. CELIA ET AL. [10] added a first-order and a zero-order term for chemistry to the transport equation, which was then solved by the localized adjoint FEM method. The reactive terms were calculated from a projection of nodal concentrations based on the previous two time steps.

Rather than adding chemistry-related terms to a transport scheme in CONTRACT-2, a classical method of lines (MOL) approach for the coupled system is used. This was applied e.g. by REICHERT [51] in a code for reactive transport problems in general aquatic environments.

The transport equation is discretized in space by an EULERIAN scheme, so that the  $n_{comp}$  PDE's for transport are transformed into a system of  $n_{comp} \cdot n_{nod}$  ODE's. These are then combined with the  $n_{nod}$  DAES's for chemistry, leading to a large DAES of order  $n_{comp} \cdot n_{nod}$ . The DAES is integrated by the solver DASPK [7].

This scheme allows consistent linearization of the entire problem. Properties of the DAES solver, such as adaptive time stepping and adaptive choice of order, are applied to the coupled set of equations. Consistent initialization must be performed only once for the entire simulation.

The computational effort of the approach is quite high, however, since large, nonlinear and stiff systems must be handled. In the decoupled approaches transport and chemistry schemes can be optimized independent of each other. As the large system of equations arising from transport is linear in these approaches, linearization concerns many small systems related to chemistry at every node. In contrast to this one large system must be linearized in the direct coupled approach, which requires longer CPU times. As less iterations are necessary, however, the overall CPU time may even be shorter than in the decoupled approach.

The resulting linear equations are highly nonsymmetric and must be solved by costly computational solvers. In CONTRACT-2 a BiConjugate Gradient solver is used. If the solver fails, a GMRES solver is used. Both solvers are available in the SLAP library [56]

## Chapter 6

# **Reactive Model Systems Recently Implemented**

### 6.1 Aerobic Degradation

Aerobic degradation is probably the most important microbial transformation process applied for bioremediation. Besides petroleum hydrocarbons such as BTEX<sup>1</sup> compounds, which are known to be highly degradable under aerobic conditions [29, 31], there have also been reports of success for many other contaminants including creosote-related compounds [32, 30].

Although for most practical applications mixtures of several contaminants must be remediated, the reactive model for aerobic degradation implemented in CONTRACT assumes a single contaminant. The model equations were taken from [2]. These are equivalent to the Equations stated in Section 2.4 with oxygen as the electron acceptor and an undefined substrate as the electron donor.

Sorption is assumed to be at equilibrium. The  $f_{OC}K_{OC}$  concept (2.3.19) is used to determine the linear partitioning coefficient  $K_d$ .

Aerobic degradation is the only transformation process considered. Biomass growth follows a double MICHAELIS-MENTEN law. Biomass grows exclusively due to the process, whilst its decay is described by a first-order expression. No transport of microbes is considered.

$$k_{gr} = \mu_{max} \frac{c_O}{c_O + K_O} \frac{c_S}{c_S + K_S}$$

$$\frac{\partial X}{\partial t} = (k_{gr} - k_{dec}) X$$
(6.1.1)

In the above expressions,  $k_{gr}$  and  $k_{dec}$  are the growth and decay coefficients for the biomass X,  $\mu_{max}$  is the maximum growth rate, and  $K_O$  and  $K_S$  are the MONOD coefficients for oxygen and the substrate, respectively.

<sup>&</sup>lt;sup>1</sup>Benzene, Toluene, Ethyl Benzene, Xylene

Reaction rates are proportional to biomass growth. For oxygen and the substrate a definition of the reactive source-sink term in the transport equation (2.2.5) is given by:

$$k_{gr} = \mu_{max} \frac{c_O}{c_O + K_O} \frac{c_S}{c_S + K_S}$$

$$r_O = -\frac{k_{gr}X}{Y_O}$$

$$r_S = -\frac{k_{gr}X}{Y_S}$$
(6.1.2)

in which  $Y_O$  and  $Y_S$  are yield coefficients.

Note that the model is based on simplifying assumptions. More sophisticated models may include NAPL dissolution [45], mass transfer kinetics [19], multiple electron acceptor utilization [39], additional limitations due to nutrient availability, transport of microbes [62, 59] or fouling of the aquifer due to microbial activity [63].

### 6.1.1 "Macrodispersion" and Bioremediation

Despite the experience gained from numereous site and laboratory studies, prediction of *in-situ* bioremediation is limited by the high uncertainty in the quantitative description of contaminant transport and transformation processes in the subsurface. The highest uncertainty may lie in microbial activity itself owing to uncertainties in the conceptual model, the need to adopt simplifying assumptions, and the fact that parameters are difficult to obtain. However, for *in-situ* applications the spatial variability of hydraulic parameters may have an even greater influence on the ability to predict bioremediation.

Various investigation techniques are available to characterize the hydraulic properties of an aquifer. Regarding the design of a bioremediation application in which the transport of compounds must be predicted, the inter-well tracer test is recommended as an appropriate site characterization technique. In this tracer test a conservative tracer is introduced into an injection well and monitored in an extraction well. The objective of this study was to interprete such tracer tests in the context of bioremediation.

Since the distribution of hydraulic properties is difficult to obtain in the field, the study was restricted to numerical modelling. Therefore, a 2-D simulation for tracer transport and biodegradation in a heterogeneous domain was carried out and taken as a reference for interpreting the data.

All of the results shown in the following Sections were obtained from CONTRACT-3. Comparative calculations using CONTRACT-FEM and CONTRACT-2, however, showed no significant differences in qualitative behaviour.

#### 6.1.1.1 Two-Dimensional Model Problem

The two-dimensional domain was a confined aquifer, 100m in length and 20m in width. The domain was divided into 100 by 40 cells over the length and width, respectively.

A stochastical distribution of hydraulic conductivities was generated with the software package GSLIB [18]. The geometric mean of hydraulic conductivity is  $10^{-3}$  m/s, with a standard deviation of logarithmic hydraulic conductivity  $\sigma_{lnk_f}$  of 1.0. This is a typical value for sandy aquifers [23]. A GAUSSIAN semivariogram with a longitudinal correlation length  $\lambda_l$  of 5m and an anisotropy factor of 2 was chosen. The generated distribution is shown in Fig. 6.1a.



Figure 6.1: (a): Two-dimensional distribution of hydraulic conductivity for the model calculation. (b): Resulting piezometric heads and pathlines; head difference between two contours: 0.05 m. (c): Snapshot of tracer distribution 20 days after start of injection.

Rather than modelling flow between two wells, a quasi-parallel flow field was investigated. This permits analytical solutions to be matched to the breakthrough curve obtained.

The hydraulic head is fixed at the left- and right-hand boundaries with a head difference of 1m. The upper and lower boundaries are impermeable. The longitudinal and transverse dispersivities are 0.01m and 0.001m, respectively. DARCY velocities vary from  $7.5 \cdot 10^{-7}$  m/s to  $9.2 \cdot 10^{-5}$  m/s. Piezometric heads and pathlines are illustrated in Fig. 6.1b. Hydraulic aquifer properties are summarized in Table 6.1.

**6.1.1.1.1 Modelling of a Conservative Tracer** A continuous tracer injection over the entire inflow boundary was simulated. The inflow concentration is homogeneous over the boundary. Fig. 6.1c shows the tracer distribution in the model aquifer 20 days after the start of injection. It is apparent that

	1 1 1		1
Geostatistical	parameters of	the hydraulic c	onductivity field
$k_f = 10^{-3} \text{ m/s}$	s $\sigma_{lnk_f} = 1.0$	$\lambda_l = 5.0 \mathrm{m}$	$\lambda_t = 2.5 \mathrm{m}$
Boundary con	ditions for the j	flow field	
h <sub>inflow</sub> - h <sub>outf</sub>	low = 1.0m		
Homogeneou	s transport prop	perties	
$n_e = 0.3$	$\alpha_l = 0.01 \mathrm{m}$	$\alpha_t = 0.001 \mathrm{m}$	$D_m = 10 - 9 \text{ m}^2/\text{s}$

Table 6.1: Hydraulic aquifer properties for the two-dimensional model problem.

the tracer is transported faster in the high permeability zones than in the low permeability zones, thus resulting in an irregular front.

In a field study the tracer distribution in the subsurface is unknown unless numereous sampling points are monitored. As a rule, only the outflow concentration in the extraction well is monitored. Integrated outflow concentrations from the numerical simulation were therefore used for the interpretation. The resulting breakthrough curve is illustrated in Fig. 6.2.



Figure 6.2: Breakthrough curve for a conservative tracer. Averaged outflow concentration based on the two-dimensional model calculation.

Breakthrough of the tracer takes place over a long period of time. Breakthrough starts at day 21 and is complete at day 50. From Fig. 6.1c it can be seen that spreading is mainly caused by spatial variations in velocity. A length profile along a single streamline would yield a tracer front extending only a few meters. The fact that the position of the front varies from streamline to streamline over a range of at least 40m reflects the distribution of hydraulic conductivity. As the transverse dispersivity is low there is little interaction between fast and slow streamtubes.

Since the breakthrough curve in Fig. 6.2 was evaluated by integration over all streamtubes, spreading occurs. This well-known scaling effect is referred to as macrodispersion [21].

**6.1.1.1.2** Modelling of Bioremediation Initial conditions for the simulation of bioremediation were specified as: homogeneous distribution of the contaminant, no oxygen present and low biomass concentrations. At time zero, water containing oxygen enters the domain. Even though oxygen is not retarded, the retardation coefficient of the substrate is 5. The parameters adopted in the model are summarized in Table 6.2. The difference in sorption behaviour is the main reason for mixing of

 Table 6.2: Microbiological parameters, including boundary and initial conditions for the two-dimensional bioremediation model.

Microbiological parameters		
$Y_O = 0.032$ $Y_S = 0.09$	$K_O = 0.2 \text{ mg/l}$	$K_S = 2.0 \text{ mg/l}$
$\mu_{max} = 5/d \qquad k_{dec} = 0.5/d$		
Sorption properties		
$f_{OC} = 0.002$ $\rho = 2600 \text{ kg/m}^3$	$K_{OC}^{S} = 330  l/kg$	$\mathbf{K}_{OC}^{O} = 0  \mathrm{l/kg}$
Boundary conditions		
Inflow concentrations	$c_O = 5 \text{ mg/l}$	$c_S = 0 mg/l$
Outflow condition	Pure advection	
Initial conditions		
$c_O = 0 \text{ mg/l}$ $c_S = 2 \text{ mg/l}$	$X = 10^{-3} mg/l$	

oxygen and the substrate. In regions where high oxygen and substrate concentrations overlap, the growth of microbial biomass occurs consuming both oxygen and the contaminant. This leads to self-sharpening of the concentration fronts.

Fig. 6.3 illustrates the distribution of concentrations 50 days after the start of injection. The effect of self-sharpening can clearly be seen: although oxygen is more mobile than the substrate, the concentration patterns show almost perfect separation. In the small mixing zone between the substrate and oxygen-containing areas microbial activity is the highest. Here the entire mass flux of oxygen is consumed.

The corresponding breakthrough curves at the outlet are illustrated in Fig. 6.4. They show no sharp fronts. Significant breakthrough of oxygen starts on day 75 and is completed by day 140. Decrease of the substrate is observed in the same time period. As in the tracer experiment, this spreading can be explained by integration over fast and slow streamtubes. Spreading of the breakthrough curves does not correspond to any mixing process on the local scale.

#### 6.1.1.2 Tracer Test Interpretation Using the Macrodispersion Model

Fitting of macro-dispersivity to the breakthrough curve was chosen as a first approach for the hydraulic characterization of the domain. This would be the first choice for most practical applications if the breakthrough curve for the tracer, the head difference between inlet and outlet and the total discharge were the only data available.

For the macrodisperion model the hydraulic conductivity was assumed to be homogeneous over the entire domain. DARCY's law was applied to determine an effective hydraulic conductivity  $k_f^e$ of  $1.09 \cdot 10^{-3}$  m/s from the total discharge, the length of the domain and the difference in hydraulic



Concentration Distribution of the Substrate [mg/L]

Figure 6.3: Two-dimensional modelling of bioremediation. Snapshot of concentration distributions 50 days after the start of injection.



Figure 6.4: Two-dimensional modelling of bioremediation. Breakthrough curves for oxygen and substrate with averaged outflow concentrations.

head between the inlet and outlet. As in the two-dimensional simulation, a uniform porosity of 0.3 was assumed in the macrodispersion model.

In the macrodispersion model spreading of the breakthrough curve is attributed to FICKIAN-type dispersion. For the given boundary conditions the model reduces to a one-dimensional advection-dispersion HEAVISIDE problem. The analytical solution for this problem by OGATHA & BANKS [48] is given in (3.6.148). A dispersivity  $\alpha$  of 2.94m was determined by a LEVENBERG- MARQUARDT algorithm implemented in the data analysis package SigmaPlot [36].



Figure 6.5: Breakthrough curve for a conservative tracer. Outflow concentration for the one-dimensional macrodospersion model compared with averaged outflow concentrations for the two-dimensional model calculation. Dispersivity  $\alpha$  = 2.94m.

Fig. 6.5 illustrates the good agreement obtained between the breakthrough curves based on the two-dimensional calculation and the macrodispersion model. The breakthrough curve based on two-dimensional modelling shows some tailing whereas the macrodisperion breakthrough curve is almost symmetrical. This difference was assumed to be of minor significance, however.

Using the macro-dispersivity parameter obtained from the tracer breakthrough curve, a simulation of bioremediation was performed. Reactive parameters as well as the boundary and initial conditions were identical to those adopted in the two-dimensional calculation.

Fig. 6.6 shows the resulting breakthrough curves for oxygen and the substrate. Unlike the two-dimensional calculations shown in Fig. 6.4, the breakthrough curve for oxygen obtained from the macrodispersion model is very sharp. Significant breakthrough starts on day 96 and is completed by day 112. Substrate concentrations also drop off more sharply.

#### 6.1.1.3 Tracer Test Interpretation Using the Two-Domain Model

The two-domain approach is described in Section 2.2.3. An analytical solution for a step-input tracer test is given by [66]. In the present study, however, the fitting parameters  $k_{m\leftrightarrow i}$  and  $n_{imm}/n_e$  were



Figure 6.6: Breakthrough curves for oxygen and substrate. Outflow concentrations for the one-dimensional macrodispersion model.

obtained by trial and error. Good agreement with the breakthrough curve obtained from the two-dimensional model was observed for  $k_{m\leftrightarrow i} = 5.8 \cdot 10^{-7}$ /s and  $n_{imm}/n_e = 0.36$ . As in the macrodispersion model, the effective hydraulic conductivity  $k_f^e$  was  $1.09 \cdot 10^{-3}$  m/s and the total porosity  $n_e$  was 0.3. The dispersivity  $\alpha$  was 0.01m. A comparison of the two breakthrough curves is illustrated in Fig. 6.7.



Figure 6.7: Breakthrough curve for a conservative tracer. Outflow concentrations for the two-domain model compared with averaged outflow concentrations for the two-dimensional model calculation. Fraction of immobile porosity  $n_{imm}/n_e = 0.36$ , mass transfer coefficient  $k_{m\leftrightarrow i} = 5.8 \cdot 10^{-7}$ /s.

Note that the results of the two-domain model agree more closely with the tracer breakthrough curve than those of the macrodispersion model, particularly with regard to tailing of the breakthrough curve. This advantage of the two-domain approach is also referred to in the literature [38].

The parameters obtained by fitting the results of the two-domain model to those of the conservative tracer test were used for simulating bioremediation. It was hereby assumed that retardation coeffi-



cients and microbiological parameters are identical in both domains.

Figure 6.8: Breakthrough curves for oxygen and substrate. Outflow concentrations obtained from the two-domain model.

Fig. 6.8 shows the resulting breakthrough curves for oxygen and the substrate. Although the breakthrough curve obtained from the two-domain model is slightly more spread out than that btained from the macrodispersion model, the extend of spreading is far less than in the case of the two-dimensional model.

#### 6.1.1.4 Tracer Test Interpretation Using the Parallel Streamtube Model

The basic assumption in the parallel streamtube model is to neglect transverse dispersivity. Solutes are thus assumed to be transported along non-interacting parallel streamtubes. Considering homogeneous effective hydraulic conductivity for each streamtube, the breakthrough curve at the outlet of the entire domain is related to the probability density function of effective hydraulic conductivity  $p(k_f^e)$  according to:

$$c(x,t) = \int_{0}^{\infty} c(x,t,k_{f}^{e}) p(k_{f}^{e}) dk_{f}^{e}$$
(6.1.3)

in which  $c(x, t, k_f^e)$  is the analytical solution for the breakthrough curve obtained for a streamtube with homogeneous effective hydraulic conductivity  $k_f^e$ . Inserting (3.6.148) into (6.1.3) yields:

$$c(x,t) = \frac{c_{in}}{2} \int_{0}^{\infty} \operatorname{erfc}\left(\frac{x - \frac{k_f^e t \Delta h}{n_e x}}{2\sqrt{\left(\frac{\alpha_l k_f^e \Delta h}{n_e x} + D_m\right)t}}\right) p(k_f^e) \, dk_f^e \tag{6.1.4}$$

In order to obtain the probability density function of effective hydraulic conductivity (6.1.4) must be inverted. The procedure may be simplified by neglecting hydrodynamic dispersion. This simplification is valid provided dispersivities are very low compared to the spreading effect of spatial variability. Note that this assumption is frequently made for the stochastical description of transport in heterogeneous porous media [17].

In this approach the breakthrough curve for the tracer reflects the distribution of arrival times  $t_{arr}$  due to advective transport in independent streamtubes [58]. Arrival times are inversely proportional to length-averaged seepage velocities and effective hydraulic conductivities.

$$c(x,t) = c_{in} \int_{0}^{t} p(t_{arr}) dt \qquad \text{with} \qquad t_{arr} = \frac{x}{v_e} = \frac{n_e x^2}{\Delta h k_f^e}$$
(6.1.5)

A tracer test based on a DIRAQ pulse would yield the non-integrated probability density function of arrival times, whereas the step-input tracer test yields the integrated probability function.

The parallel streamtube concept was used for predicting bioremediation using the following procedure:

1. Given the conservative tracer breakthrough curve, normalize the breakthrough curve on the basis of the inflow concentration.

$$\tilde{c} = c/c_{in}$$

2. Convert travel times into length-averaged seepage velocities and effective hydraulic conductivities.

$$v_e = \frac{x}{t_{arr}} \qquad \qquad k_f^e = \frac{n_e x^2}{\Delta h t_{arr}}$$

- 3. Divide the resulting probability function  $\tilde{c}(k_f^e)$  into classes.
- Calculate bioremediation for every class of effective hydraulic conductivity assuming the midpoint value of each class to represent homogeneous hydraulic conductivity and neglecting dispersion.
- 5. Weight the obtained breakthrough curves with the probability of the class.
- 6. Summate all weighted breakthrough curves to obtain the final prediction of reactive breakthrough.

Fig. 6.9 illustrates the breakthrough curves for oxygen and the substrate for a single streamtube with hydraulic conductivity of  $10^{-3}$  m/s, which is equivalent to a seepage velocity of  $3.3 \cdot 10^{-5}$  m/s. The curve shows a first oxygen peak around day 33, reflecting initial breakthrough after one pore volume. The low initial biomass in the system limits oxygen consumption until biomass has grown, thus allowing a slowly decreasing oxygen peak to move through the domain [13]. The final breakthrough of oxygen around day 110 corresponds to a sharp decrease in substrate concentrations, thereby indicating remediation of the aquifer.



Figure 6.9: Breakthrough curves for oxygen and substrate. Outflow concentrations for a single one-dimensional stream-tube with a hydraulic conductivity of  $10^{-3}$  m/s.



Figure 6.10: Probability of effective hydraulic conductivity classes resulting from interpretation of the tracer breakthrough curve.

Fig. 6.10 illustrates the probability of effective hydraulic conductivity classes in independent parallel streamtubes obtained by the procedure explained above. Note that this distribution is not the real distribution of  $k_f$  for the two-dimensional calculation. The distribution of Fig. 6.10 was obtained without any knowledge of the real parameter field. The real distribution of  $k_f$  is likely to be more widespread, since  $k_f^e$  is an effective parameter averaged over the length of the streamtube.

Bioremediation was simulated for all the 20 classes shown in Fig. 6.10. The resulting breakthrough curves were weighted with the probability of the classes and summated thus leading to the break-through curves illustrated in Fig. 6.11.



Figure 6.11: Breakthrough curves for oxygen and substrate. Outflow concentrations integrated over all weighted onedimensional streamtubes with the hydraulic conductivity distribution as shown in Fig. 6.10.

A comparison of the reactive breakthrough curves given by the parallel streamtube model to those obtained from the two-dimensional model shows rather fair agreement. In contrast to the macrodispersion and the two-domain model, spreading of the breakthrough curves is in the correct range. Total remediation of the aquifer was achieved after 140 days and 150 days in the case of the twodimensional model and the parallel streamtube model, respectively. This difference may be due to the neglection of transverse mixing in the parallel streamtube model.

#### 6.1.1.5 Discussion

It it apparent that both the macrodispersion model and the two-domain model give inadequate predictions of bioremediation if their hydraulic parameters are obtained by fitting breakthrough curves for a conservative tracer.

In the two-dimensional calculation the compounds are not mixed due to spatial variability. Spatial variability leads to irregular-shaped but sharp fronts. Integrating over the cross-section at the outlet of the domain leads to spreading in the breakthrough curve. This spreading does not reflect local-scale mixing processes.

Although the distinction between local-scale mixing and large-scale spreading is not necessary for

describing conservative tracer transport, it is necessary for the transport of interacting compounds [65]. As microbial activity takes place on the local scale, oxygen and the substrate must thus be mixed on the local scale to stimulate the latter. Compounds in parallel streamtubes cannot react unless they are mixed by transverse exchange.

In the macrodispersion model the effect of local-scale spatial variability on large-scale behaviour is modelled as diffusion. As a consequence, oxygen and the substrate are mixed and react with each other. This reaction leads to self-sharpening of the fronts.

In the two-domain model the same process is modelled as kinetic sorption. Although kinetic mass transfer is viewed as a possible limitation for bioremediation under certain circumstances [5], it results in a mixing process in the context of the stated model problem and may therefore enhance biodegradation.

Both the macrodispersion model and the two-domain model do not distinguish between local-scale mixing and spreading due to integration over the cross-section of the domain. One may assume that this is an effect of dimensionality, since a two-dimensional problem is solved by a one-dimensional model. However, the boundary conditions imply one-dimensional treatment. In [43] it was shown that a two-dimensional macrodispersion model for biodegradation in an aquifer differs from a model based on a heterogeneous hydraulic conductivity distribution. Therefore the most signifant simplification of the macrodispersion and two-domain models is that a heterogeneous problem is treated as a homogeneous one.

In the context of perturbation theory this may be interpreted as an anticorrelation effect. Simplifying the reaction rate to a term proportional to the product  $c_O \cdot c_S$  and dividing these concentrations into width-averaged values  $\overline{c_O}$ ,  $\overline{c_S}$  and deviations from these averages  $c'_O$ ,  $c'_S$  yields:

$$r \sim \frac{\overline{c_O \cdot c_S}}{\overline{c_O} \cdot \overline{c_S}} = \frac{\overline{(\overline{c_O} + c'_O)} \cdot (\overline{c_S} + c'_S)}{\overline{c_O} \cdot \overline{c_S}} = \overline{\overline{c_O} \cdot \overline{c_S}} + \overline{c'_O \cdot \overline{c_S}} + \overline{\overline{c_O} \cdot c'_S} + \overline{c'_O \cdot c'_S} = (6.1.6)$$

where the correlation term  $\overline{c'_O \cdot c'_S}$  is negative for the given model problem. Therefore reaction rates are overestimated by models based on width-averaged tracer data.

The parallel streamtube model overcomes this problem. Concentrations are not averaged over the cross-section of the domain until they reach the outlet. Since local dispersivities are quite low, and mixing is dominated by differences in the sorption properties of the two compounds, the assumption of pure advective transport is qualitatively valid.

However, local-scale mixing is not completely independent of spatial variability. Scaling laws for mixing as given in [65] require geostatistical parameters of the hydraulic conductivity field. It is not possible to derive local-scale mixing coefficients from macro-dispersivity, since macro-dispersivity increases with increasing correlation length whereas mixing decreases with increasing correlation lengths.

For the parallel streamtube model hydraulic conductivity was assumed to be homogeneous in each streamtube. Considering the real distribution of hydraulic conductivity in the two-dimensional model, this assumption is not valid. However, the variation of hydraulic conductivity along a streamtube can-

not be derived from the tracer test data. For the stated model problem this simplification introduced no significant error. This may be different if non-linear or kinetic mass transfer processes are considered.

The geometry and boundary conditions of the model problem are unrealistic for practical applications. For an inter-well tracer test a three-dimensional divergent/convergent flow field has to be considered. However, if the length of the streamtubes do not differ too much, the parallel streamtube model may be directly used for more complex geometries, assuming an averaged length for all streamtubes. The concept may be modified by assuming idealized homogeneous horizontal layers with different homogeneous hydraulic conductivities. In this context (6.1.3) has to be inverted using the analytical or numerical solution of arrival times for an injection-extraction well couple rather than for a one-dimensional streamtube.

#### 6.1.1.6 Concluding Remarks

Macrodispersion or large-scale spreading, and local-scale mixing are two different processes which should not be confused. If integrated data obtained for example from pumping tests and inter-well tracer tests are the only available data for the hydraulic characterization of an aquifer, the parallel streamtube concept may give the best interpretation for predicting the transport of interacting compounds.

A problem which has not been addressed in this study arises from the unknown distribution of the contaminant. For the model calculations a homogeneous substrate distribution was assumed. For most practical applications the contaminant will not be equally distributed over high and low permeability areas, and hence a correlation between contamination and hydraulic conductivity would have to be considered for the evaluation of scaling laws.

Whereever possible, the true spatial distribution of hydraulic parameters should be investigated. Distributed data are preferable to integrated data in the context of reactive transport. Latest developments in geophysical site characterization techniques such as electrical tomography applied to salt tracer tests raise hopes that high resolution hydraulic characterization may be achieved without taking numereous samples. However, a prediction of bioremediation is dependent on the hydraulic and microbiological characterization of the process itself. Uncertainties in the description of microbial transport, degradation kinetics and mixed-culture microbial ecology limits the prediction of bioremediation. At the current state-of-the-art numerical simulation may be considered as a tool for the interpretation of measured data and the identification of relevant processes in coupled problems rather than as a tool for reliable predictions.

## 6.2 Reductive Dechlorination of Tetrachloroethene

Chlorinated ethenes are among the most important contaminants in the subsurface due to their widespread use as solvents. Until the mid-80's chlorinated hydrocarbons were believed to be non-biodegradable. This is certainly in the case of aerobic degradation of highly chlorinated hydrocarbons such as tetrachloroethene (PCE). Yet these contaminants were found to be degradable under reductive conditions [68]. Fig. 6.12 shows the pathway for complete reductive dechlorination of PCE. The chlorinated ethenes act as electron acceptors while the electron donor can be as shown in Fig. 6.12 molecular hydrogen or other compounds such as glucose, formate, methanol, lactate, propionate or ethanol. This variety might be explained by the initial transformation of these compounds to molecular hydrogen, which acts then as the direct reducing compound for the chlorinated ethenes [60].



Figure 6.12: Degradation pathway for reductive dechlorination of tetrachloroethene (PCE).

Note that the first two reduction steps are preferred not only due to the higher free enthalpy of reaction but also due to kinetic effects. Although several successful isolations of microorganisms catalyzing the first two reactions are reported in the literature [34, 54], no pure culture has yet been isolated which is capable of catalyzing the entire reduction chain.

Up to now we do not konw, how many microbes actually participe in the complete reductive dechlorination of PCE. There is strong evidence that at least two organisms are necessary. The model system is therefore simplified for one specific type of biomass  $X^i$  per reduction step. These biomasses are model measures which need not necessarily reflect specific organisms.

The work of SCHOLZ-MURAMATSU ET AL.[54] in particular indicates that dechlorinating organisms can grow specifically on the dechlorination process. As a consequence, the model assumes that the specific biomasses grow exclusively on reductive dechlorination. For this reason double MONOD terms are adopted to express the dependence of biomass growth on concentrations (6.2.7).

$$k_{gr}^{i} = \mu_{max}^{i} \frac{[CHC_{i}]}{[CHC_{i}] + K_{m}^{CHC_{i}}} \cdot \frac{[E_{don}]}{[E_{don}] + K_{m}^{E_{don}}} [X^{i}]$$
(6.2.7)

in which  $k_{gr}^i$  is the growth rate of biomass  $X^i$ ,  $\mu_{max}^i$  is its maximum relative growth rate,  $CHC_1$  is tetrachloroethene (PCE),  $CHC_2$  is trichloroethene (TCE),  $CHC_3$  is *cis*-dichloroethene (DCE),  $CHC_4$  is chloroethene (VC) and  $CHC_5$  is ethene (ETH),  $E_{don}$  is a non-specified electron donor,  $X^1$  is the biomass catalyzing the reduction from PCE to TCE,  $X^2$  catalyzes the reduction from TCE to DCE,  $X^3$  catalyzes the reduction from DCE to VC, and  $X^4$  catalyzes the reduction from VC to ETH.

The reactive source-sink terms  $r_i$  in the transport equation (2.2.5) are defined for the mobile compounds by adding the microbial consumption and production terms to a kinetic mass transfer term:

$$r_{E_{don}} = -\sum_{i=1}^{4} \frac{k_{gr}^{i}}{Y_{i}} - k_{comp}[E_{don}] - k_{sorb} \left( [E_{don}] - \frac{[E_{don}^{sorb}]}{K_{d}^{E_{don}}} \right)$$
(6.2.8)

$$r_{CHC_i} = -\frac{k_{gr}^i}{Y_i} + \frac{k_{gr}^{i-1}}{Y_{i-1}} - k_{sorb} \left( [CHC_i] - \frac{[CHC_i^{sorb}]}{K_d^{CHC_i}} \right)$$
(6.2.9)

in which  $Y_i$  are yield coefficients for the reduction step *i*. Note that in the model one molecule of  $E_{don}$  is oxidized by one molecule of  $CHC_i$ . For different stoicheometry, additional factors have to be included.

The first term in (6.2.8) reflects additional competitive consumption of the electron donor expressed by simple first-order kinetics.  $k_{comp}$  is the coefficient of first-order decay due to this process.

For reasons of simplification the sorbed concentrations are related to the liquid volume. Kinetic mass transfer is the only process considered for sorbed compounds:

$$\frac{\partial [CHC_i^{sorb}]}{\partial t} = k_{sorb} \left( [CHC_i] - \frac{[CHC_i^{sorb}]}{K_d^{CHC_i}} \right)$$
(6.2.10)

$$\frac{\partial [E_{don}^{sorb}]}{\partial t} = k_{sorb} \left( [E_{don}] - \frac{[E_{don}^{sorb}]}{K_d^{E_{don}}} \right)$$
(6.2.11)

The development of biomasses is expressed by the growth term of (6.2.7) and a linear decay term:

$$\frac{\partial[X^i]}{\partial t} = k^i_{gr} - k^i_{dec}[X^i]$$
(6.2.12)

#### 6.2.1 Comparison of Batch Experiments and 1-D Reactive Transport

Classical microbiological laboratory studies on biodegradation are carried out in mixed systems. These can be batch experiments in which all substrates are introduced into the reactor at the start of the experiment, or continuous stirred reactor experiments in which substrates are added continuously or in pulses. The objective of these studies is to determine degradation pathways as well as degradation kinetics and their relationship to chemical and microbial parameters such as type and concentration of substrates and biomass.

In the context of bioremediation these studies are carried out using soil material from a contaminated site. These give an indication as to whether indigenous microbes capable of degrading the contaminants are present and what kind of chemical environment they require for optimal stimulation. However, as shown in the present study, successful stimulation in a batch experiment is no guarantee for a successful *in-situ* application.

Note that the experiments in the present study are numerical simulations. Although the numerical simulations of batch experiments yield results in good agreement with laboratory experiments [55], the underlying conceptual and/or mathematical model may be erroneous. Therefore this study should be viewed as an illustration of system behaviour rather than as a quantitative prediction of *in-situ* dechlorination.

In this study a batch system is compared to a one-dimensional reactive transport system. The results of a two-dimensional simulation can be found in [12].

#### 6.2.1.1 Modelling of Batch Experiments

In order to make comparisons as easily as possible most parameters were identical in the batch model and the 1-D model. This includes porosity, even though in bioreactor studies the soil would be dilluted to a slurry. The model equations are described above. Parameters are summarized in Table 6.3. The kinetic parameters for the first two reduction steps lie within the range of values obtained in [54] for laboratory studies using a pure culture. The kinetic parameters for dechlorination steps 3 and 4 are extrapolations based on the experience that dechlorination rates decrease with decreasing number of chloro groups in the molecule [68].

For the batch experiments an initial electron donor concentration of 10 mmol/L was chosen. PCE was the only ethene derivative present at a concentration of 200  $\mu$ mol/L in equilibrium with the sorbed phase. Initial biomass concentrations were low (0.01 mg/L). The mass transfer coefficient was set to a moderate value of 1/day.

Table 6.3: Parameters for the model calculations of the test case.						
Compound related parameters						
	$\mathbf{E}_{don}$	PCE	TCE	cis-DCE	VC	ETH
$\mathrm{K}_{m}^{i}$ [ $\mu \mathrm{mol}/\mathrm{L}$ ]	100	100	100	100	100	100
$\mathbf{K}_{OC}^{i}$ [L/kg]	2.2	364	126	59	8.2	6.0
$k_{comp}$ [1/s]	$10^{-6}$					
Biomass related parameters						
	Step 1	Step 2	Step 3	Step 4		
$\mu_{max,i}$ [1/s]	$7.7 \cdot 10^{-5}$	$5.0 \cdot 10^{-5}$	$2.5 \cdot 10^{-5}$	$1.0 \cdot 10^{-5}$		
$Y_i [mg/\mu mol]$	0.001	0.001	0.001	0.001		
$k_{dec}$ [1/s]	$1.0 \cdot 10^{-6}$	$1.0\cdot10^{-6}$	$1.0\cdot10^{-6}$	$1.0 \cdot 10^{-6}$		
$X_{initial}$ [mg/L]	0.01	0.01	0.01	0.01		
Soil properties						
$\rho = 2.6$ kg/L	$f_{OC} = 0.2\%$	)	$n_e = 0.3$	$k_{sorb} = 1/d$	= 1.15	$57 \cdot 10^{-5}/s$

Fig. 6.13 shows the time profiles of all dissolved compounds. It is apparent that dissolved PCE is consumed very fast being visually undetectable after 2 days. TCE is the first metabolite and is also consumed quite fast. On day 4 almost no dissolved TCE is detectable. The second metabolite in the reduction chain is *cis*-DCE which persists in the dissolved phase for about one week. The third dechlorination product VC persists much longer. Around day 12 it is visually undetectable. However, the overall dechlorination is not yet complete as the dissolved ethene concentrations continues to increase until the end of the simulation on day 20.

The electron donor is partly consumed by the dechlorination process and partly by the competitive first-order process. However, the initial concentration was chosen high enough to guarantee complete reductive dechlorination. This was not the case for a simulation in which the initial electron donor concentration was set to 1 mmol/L.

Fig. 6.14 shows the time profiles of all sorbed compounds. In contrast to the dissolved phase, PCE remains in the sorbed phase over the entire duration of the simulation. This is an effect of kinetic desorption. The effects of desorption kinetics have less influence on the time profiles for the other sorbed chlorinated ethenes. Note that the definition of the mass transfer term in (6.2.10) leads to a half-life for desorption proportional to the partitioning coefficient  $K_d$ . As  $K_d$  values decrease with decreasing chlorination of ethene, desorption of PCE is limited to a greater extend by kinetics than TCE, DCE and VC. The TCE<sup>sorb</sup> time profile still shows extensive tailing, whereas tailing of the DCE<sup>sorb</sup> profile is much weaker. In the case of VC<sup>sorb</sup>, hardly any tailing occurs.

Fig. 6.15 shows time profiles for the biomasses. Differences in growth are apparent which reflect the availability of the corresponding electron acceptor (= the chlorinated ethene degraded by the type of biomass) and mainly the maximum growth rate. In particular, the relationship between biomass growth and electron acceptor concentration can clearly be seen for the biomass catalyzing the last reduction step. From day 11 onwards dissolved VC concentrations are very low. This is the time when the decay of biomass 4 exceeds growth.

Summarizing Figs. 6.13-6.15 lead to the following conclusions:



Figure 6.13: Reductive dechlorination of PCE. Model calculation of a batch test. Time profiles of dissolved compounds.



Figure 6.14: Reductive dechlorination of PCE. Model calculation of a batch test. Time profiles of sorbed compounds.



Figure 6.15: Reductive dechlorination of PCE. Model calculation of a batch test. Time profiles of biomasses.

- 1. Complete reductive dechlorination can be achieved in 20 days.
- 2. If the initial electron donor concentration is high enough, limitations due to competitive consumption of the electron donor can be avoided.
- 3. Differences in maximum biomass growth and related dechlorination rates for the different dechlorination steps lead to longer persistence of the lower chlorinated ethenes than the higher chlorinated ethenes.
- 4. From day 11 onwards the complete reduction chain is controlled by desorption kinetics of PCE. During this period the dissolved concentrations are so small that biomass decay exceeds growth for all types of biomass. Nevertheless, the remaining biomass concentrations are high enough to guarantee rapid transformation of dissolved PCE into ethene.

#### 6.2.1.2 Modelling of Reductive Dechlorination Coupled to One-Dimensional Transport

The parameters in the batch experiment (Table 6.3) were adopted for the simulation of reactive transport in a one-dimensional streamtube of 100m length. The DARCY velocity  $\vec{v}$  was  $10^{-5}$  m/s with a dispersivity of 0.01m, corresponding to an effective diffusion coefficient of  $3.3 \cdot 10^{-7}$ m<sup>2</sup>/s. Homogeneous contamination of the domain by 200  $\mu$ mol/L PCE was chosen as the initial condition in the absence of any other ethene derivative or electron donor. The input concentration of the electron donor was 10 mmol/L.

Fig. 6.16-6.19 show length profiles of the dissolved compounds obtained from CONTRACT-2. The

model was used to compare different coupling schemes. As reported in [15], no significant differences could be observed between the results obtained from CONTRACT-FEM, CONTRACT-2 or CONTRACT-3.



Figure 6.16: Reductive dechlorination of PCE in a 1-D model system. Concentration length profiles of dissolved compounds 10 days after the electron donor injection.



Figure 6.17: Reductive dechlorination of PCE in a 1-D model system. Concentration length profiles of dissolved compounds 20 days after the electron donor injection.



Figure 6.18: Reductive dechlorination of PCE in a 1-D model system. Concentration length profiles of dissolved compounds 30 days after the electron donor injection.



Figure 6.19: Reductive dechlorination of PCE in a 1-D model system. Concentration length profiles of dissolved compounds 40 days after the electron donor injection.

The length profiles of Fig. 6.16-6.19 indicate that the entire mass flux of the electron donor is consumed in a small mixing zone where the electron donor and all chlorinated ethenes are present. Due to the first order decay an exponential length profile develops between the system inlet and the reactive mixing zone.

10 days after start of injection (see Fig. 6.16) the peaks of all ethenes overlap. All chlorinated ethenes are thus mixed with the electron donor, thereby stimulating growth of the reducing biomasses. Although ethene is the compound with the highest solubility in water its concentrations are the lowest. This is an effect of the low transformation rates from VC to ethene.

The mobility of the chlorinated ethenes increases with decreasing chlorination. As a consequence, VC advances faster than the other chlorinated compounds. Already after 20 days (see Fig. 6.17) a separation of the VC peak can be observed. This has dramatic consequences for the ability to reduce VC since the VC peak moves out of the region where the electron donor is available. As can be seen in Fig. 6.18 and 6.19 the VC peak remains unchanges up to the end of the simulation on day 40.

Note that the transformation rates of reductive dechlorination and the related growth rates of the responsible biomasses decrease with decreasing chlorination. Together with the increasing mobility this leads to a limitation of complete reductive dechlorination. The reduction of low chlorinated ethenes requires a longer mixing time with the electron donor than the reduction of highly chlorinated ethenes. Due to their higher mobility, however, they are mixed for a shorter time. An accumulation of DCE and VC thus occurs.

#### 6.2.1.3 Discussion

The qualitative behaviour of reductive dechlorination is different between a batch system, as shown in Section 6.2.1.1, and a reactive transport system, as shown in Section 6.2.1.2. Complete reduction can be achieved in a batch system if the initial electron donor concentrations are high enough, whereas reductive dechlorination is not complete in the case of reactive transport.

This is clearly an effect of the interaction between mixing and mobility. As the metabolites are more mobile than the original contaminant and the electron donor is completely consumed in a small mixing zone, the fast moving metabolites tend to move out of the reactive region.

Kinetic sorption, which was limiting in the case of the mixed reactor, may enhance mixing of the electron donor and the metabolites and therefore enhance complete reductive dechlorination.

Note that the assumption of increasing mobility with decreasing chlorination is based on the premise that sorption controls mobility. This needn't be the case in reductive systems. Methanogenesis can lead to entrapped gas bubbles in highly reductive aquifers. Since the volatility of the chlorinated ethenes increases with decreasing chlorination the mobility may increase as well in highly reductive systems. In this case the separation of a fast moving VC peak would not take place. In fact, complete reductive dechlorination in the field has been reported mostly for methanogenic aquifers [57].

# Appendix A

# **Description of Input Files**

The name of the input files must have the extension \* . cmd. The files may be structured using comment lines. Comment lines can be inserted at anywhere exept in the first line containing the header. A comment line is marked by "C" in the first column.

Note, that the variable names are identical to the variable names in the source code and correspond to German expressions.

## A.1 CONTRACT-FEM

CONTRACT-FEM requires the solution of the flow field by the flow model ROCKFLOW-SM2 [69]. Flow parameters as well as geometry and grid informations must be defined in the SM2 input files. A description of the corresponding file format is given in [70]. Note that data exchange between ROCKFLOW-SM and CONTRACT-FEM is performed using binary files.

#### I. Header

Column	Variable	Туре	Comment
1-80	UEB	CHARACTER*80	Header;
			appears in all output files

#### II. Main Control Lines

#### II.1. First Main Control Line

Column	Variable	Туре	Comment
1-5	FLG	INTEGER	(1)
6-15	TSTART	REAL	(2)
16-20	NZKURV	INTEGER	(3)

21-25	RESTART	INTEGER	(4)
26-30	CHEMART	INTEGER	(5)
31-35	DCHECK	INTEGER	(6)
35-40	VM	INTEGER	(7)
41-45	BATCH	INTEGER	(8)
46-55	TINT	REAL	(9)
56-60	MSTR	INTEGER	(10)
61-65	GSSFLG	INTEGER	(11)
66-75	RELAX	REAL	(12)

(1) Flag for time step control

FLG = 1:	Steady state flow, constant time steps for transport;
	Requires 1 control line of type A
FLG = 2:	variable time steps for transport;
	Requires control lines of types B,C and D
	(see program manual of SM)
FLG = 3:	Time stepping controlled by flow model SM
FLG = 4:	Internal Flag
FLG = 5:	Time step control starting at TSTART
FLG = 6 :	Steady-state

- (2) Starting time of simulation
- (3) Number of time curves for transient boundary conditions
- (4) **RESTART-Flag**

RESTART = 0:	Normal calculation
RESTART = 1:	RESTART of previous calculation

(5) Flag for chemistry model

CHEMART = 0:	No chemistry; sorption at equilibrium
CHEMART = $1$ :	Aerobic degradation; sorption at equilibrium
CHEMART = $2$ :	No chemistry; two-domain approach
CHEMART $= 3$ :	Reductice dechlorination of PCE
CHEMART = 4:	Aerobic degradation + two-domain approach

(6) Flag for check run

DCHECK = 0:	Normal run
DCHECK = 1:	Data check

(7) Control parameters for velocity model

VM = 0:	Velocity field calculated by flow model SM
VM = 3 :	Counterclockwise rotation
# A.1. CONTRACT-FEM

	VM = 4 :	Parallel flow	
(8)	Batch run ?		
	BATCH = 0: BATCH = 1:	No Yes	
(9)	Time discretization for out	put	
	TINT = 0.0 : Every time st	ep is protocoled	
(10)	*.cme output		
	MSTR = 0 : MSTR = 1 : MSTR = 2 :	Output of concentrati Output of concentrati No *.cme output	ons and mass fluxes in *.cme ions only
(11)	Flag for GSS or TECPLOT output		
	GSSFLG $i_0 0$ : GSSFLG = 1 : GSSFLG = 2 : GSSFLG = 3 : GSSFLG = 4 :	No GSS-file GSS-file in ASCII Binary GSS-file GSS-file in encoded-A output in TECPLOT-f	ASCII format
(12)	Relaxation factor		
II.2.	Second Main Control Lir	ıe	
Column 1-9 11-15 16-20 21-25 26-30 31-40	Variable THETA MLSXCH UPMETH IPLG IWFO THELO	Type REAL INTEGER INTEGER INTEGER REAL	Comment (1) (2) (3) (4) (5) (6)

		<b>7</b> I	
1-9	THETA	REAL	(1)
11-15	MLSXCH	INTEGER	(2)
16-20	UPMETH	INTEGER	(3)
21-25	IPLG	INTEGER	(4)
26-30	IWFO	INTEGER	(5)
31-40	THELO	REAL	(6)
41-45	MLLO	INTEGER	(7)
46-50	UPLO	INTEGER	(8)
51-60	THEHI	REAL	(9)
61-65	MLHI	INTEGER	(10)
66-70	GSSFLG	INTEGER	(11)

Weighting of implicit terms in time discretization (1)

THETA = 0	: Fully explicit
THETA $= 0.5$	: Crank-Nicolson integration
THETA $= 1$	: Fully implicit
If FLG=6 then THETA=1	

(2) Flag for mass lumping

MLSWCH = 0:	No mass lumping
MLSWCH = 1:	Mass lumping

(3) Upwinding method

UPMETH = 0:	Standard Galerkin method
UPMETH $= 1$ :	Taylor-Galerkin method
UPMETH = $2$ :	Standard-Galerkin with artificial longitudial diffusion
UPMETH $= 3$ :	N+1 Upwinding after Hayakorn & Nilkuha
UPMETH = $4$ :	N+1 Upwinding with $\alpha_{opt}$ for steady state
UPMETH $= 5$ :	N-1 Upwinding with $\alpha_{opt}$ for steady state
UPMETH = $6$ :	Flux-Corrected-Transport (FCT)
UPMETH $= 7$ :	FEM Control Volume "9 Point" differentiation
UPMETH $= 8$ :	FEM Control Volume "5 Point" differentiation

(4) Flag for solver of linear system of equations

IPCG = 0:	Skyline method
IPCG = 1:	PCG method

(5) Flag for weak formulation

IWFO = 0:	Advective mass flux by strong formulation
IWFO = 1:	Advective mass flux by weak formulation

- (6) (11) are only needed if UPMETH = 6
- (6)  $\Theta$  of low-order method
- (7) MLSWCH of low-order method
- (8) UPME of low-order method
- (9)  $\Theta$  of high-order method
- (10) MLSWCH of high-order method
- (11) UPME of high-order method

# II.2.A. Control Line of Type A

Column	Variable	Туре	Comment
1-5	ANZDT	INTEGER	Number of timesteps to be
	$(ANZDT_{\dot{c}}0)$		calculated
6-15	DT	REAL	Timestep increment

#### A.1. CONTRACT-FEM

 $(DT_{c}; 0)$ 

For FLG = 2 any number of periods with any number of time steps of constant size can be defined

# **II.2.B.** Control Line of Type B

Column 1-5	Variable NPER	Type INTEGER	Comment Number of periods with constant time step	
II.2.C.	Control Line of Type C			
Column 1-5 6-10 	Variable NSPER(1) NSPER(2) NSPER(NPER)	Type INTEGER INTEGER INTEGER	Comment NPER entries for number of time steps in corresponding period	
II.2.D.	Control Line of Type D			
Column 1-10 11-20  <b>II.2.</b>	Variable DTPER(1) DTPER(2) DTPER(NPER) <b>Third Main Control Line</b>	Type REAL REAL REAL	Comment NPER entries for length of time steps in corrsponding period. Maximum number of entries per line : 8	
Column 1-5 6-10	Variable ANZMOB ANZIMM	Type INTEGER INTEGER	Comment Number of mobile components Number of immobile components ANZKOM = ANZMOB + ANZIMM	

# III. Time Curves

These lines are skipped for NZKURV=0. Each time curve requires at least three lines. Time curves are described by polygons. Values between two points in the time curve are evaluated by linear interpolation.

III.1.	Line 1		
Column	Variable	Туре	Comment
1-5	IPKT	INTEGER	Number of points describing the
			time curve
III.2.	Line 2		
Column	Variable	Туре	Comment
1-10	ZEIT(1)	REAL	Entries for time values of the points
11-20	ZEIT(2)	REAL	describing the time curve.Maximum
	ZEIT(IPKT)		number of entries per line : 8.
			For IPKT¿8 a second (third) line
			has to be added.

# III.3. Line 3

Column	Variable	Туре	Comment
1-10	FAKTOR(1)	REAL	Entries for factor values
11-20	FAKTOR(2)	REAL	corresponding to the
	FAKTOR(IPKT)		time values

# IV. Outflow Nodes

Column	Variable	Туре	Comment
1-5	NO	INTEGER	Number of outflow nodes
6-10	KN	INTEGER	corresponding node numbers

# V.1. Name and Accuracy of each Component

Column	Variable	Туре	Comment
1-10	NAME	CHARACTER	Name of component
11-15	CMIN	INTEGER	Minimum concentration
16-20	CMAX	INTEGER	Maximum concentration
21-25	RELFEHL	INTEGER	Maximum relative error
26-30	ABSFEHL	INTEGER	Maximum absolute error
31-35	CDEF	INTEGER	Standard initial concentration
36-40	KOC	INTEGER	Partitioning coefficient between
			organic carbon and water

#### V.2. Number of Initial and Boundary Conditions

Column	Variable	Туре	Comment
1-5	NC	INTEGER	(1)
6-10	NR	INTEGER	(2)
11-15	NQ	INTEGER	(3)

- (1) Number of nodes with special initial values. Initial values at all other nodes are set to CDEF.
- (2) Number of nodes with fixed concentrations.
- (3) Number of nodes with definite inflow concentration.

# VI. Initial Conditions

Column	Variable	Туре	Comment
1-5	KN	INTEGER	Node number
6-15	С	REAL	Initial Concentration

Comment: If NC¿0 there are NC lines of this type needed.

#### A.1. CONTRACT-FEM

# **VII.** DIRICHLET **Boundary Conditions (Fixed Concentration)**

Column	Variable	Туре	Comment
1-5	KN	INTEGER	Node number
6-10	ZK	INTEGER	(1)
11-20	R	REAL	Boundary condition at node KN
21-25	INKR	INTEGER	(2)

 Number of Time Curve ZK=0 : Constant fixed concentration of value R. ZK<sub>i</sub>0 : Transient boundary condition. The fixed concentration is evaluated by multiplication of R with the time curve.
 Increment for DIRICHLET boundary condition

NR lines of this type are required.

# VIII. Inflow Boundary Condition

Column	Variable	Туре	Comment
1-5	KN	INTEGER	Node number
6-10	ZK	INTEGER	(1)
11-20	Cin	REAL	Inflow concentration at node KN

(1) *Number of Time Curve* 

ZK=0 : Constant fixed concentration of value R.
 ZK<sub>i</sub>0 : Transient boundary condition. The fixed concentration is evaluated by multiplication of Cin with the time curve.

# IX. Soil Properties

#### IX.1. Porosity and Diffusion/Dispersion Parameters

a)Flow elements (1-D)

Column	Variable	Туре	Comment
1-10	POROS	REAL	(1)
11-15	MNR	INTEGER	(2)
16-25	alpha_1	REAL	Longitudinal dispersivity
26-35	D_molek	REAL	Molecular diffusion coefficient
36-45	CORG	REAL	Mass fraction of organic carbon in
			dry soil
46-55	TORT	REAL	Tortuosity (Default:1.0)
56-65	FDICH	REAL	Density of rock matrix

b) Flow elements (2-D)

Column	Variable	Туре	Comment
1-10	POROS	REAL	Porosity
11-15	MNR	INTEGER	Dispersion model(1)
16-25	alpha_1	REAL	Longitudinal dispersivity
26-35	alpha_2	REAL	Transverse dispersivity
36-45	D_molek	REAL	Molecular diffusion coefficient
46-55	CORG	REAL	Mass fraction of organic carbon in
			dry soil
56-65	TORT	REAL	Tortuosity (Default:1.0)
66-75	FDICH	REAL	Density of rock matrix

(1) *Model 1: Isotropic diffusion, no dispersion Model 2: SCHEIDEGGER parametrization of effective diffusion* 

# X. Chemistry-Related Parameters

For CHEMART=0 the following lines can be skipped.

a) CHEMART = 1

Aerobic degradation, sorption at equilibrium.

Column	Variable	Туре	Comment
1-10	MUEMAX	REAL	(1)
11-20	YIELDS	REAL	(2)
21-30	YIELDO	REAL	(3)
31-40	KS	REAL	(4)
41-50	KO	REAL	(5)
51-60	KSTERB	REAL	(6)

- (1) *Maximum growth rate* [1/s]
- (2) *Yield coefficient of substrate* [mg/mg]
- (3) *Yield coefficient of oxygen* [mg/mg]
- (4) MONOD *coefficient of substrate* [mg/L]
- (5) MONOD *coefficient of oxygen* [mg/L]
- (6) *Decay rate of biomass* [1/s]

#### a) CHEMART = 2

Two-domain approach - no chemical transformations.

Column	Variable	Туре	Comment
1-10	NIMM	REAL	Ratio of immobile to total porosity [-]
11-20	ALPHAS	REAL	Mass transfer coefficient [1/s]

#### A.1. CONTRACT-FEM

#### b) CHEMART = 3

Reductive dechlorination of Tetrachloroethene - kinetic sorption.

#### X.c.1. First Line

Column	Variable	Туре	Comment
1-10	MUEMAX(1)	REAL	(1)
11-20	MUEMAX(2)	REAL	(2)
21-30	MUEMAX(3)	REAL	(3)
31-40	MUEMAX(4)	REAL	(4)

- (1) *Maximum growth rate of biomass 1* [1/s]
- (2) *Maximum growth rate of biomass* 2 [1/s]
- (3) *Maximum growth rate of biomass 3* [1/s]
- (4) *Maximum growth rate of biomass 4* [1/s]

#### X.c.2. Second Line

Column	Variable	Туре	Comment
1-10	YIELD(1)	REAL	(1)
11-20	YIELD(2)	REAL	(2)
21-30	YIELD(3)	REAL	(3)
31-40	YIELD(4)	REAL	(4)

(1)	Yield coefficient	of biomass 1	[mg/mol]
-----	-------------------	--------------	----------

- (2) *Yield coefficient of biomass* 2 [mg/mol]
- (3) *Yield coefficient of biomass 3* [mg/mol]
- (4) *Yield coefficient of biomass 4* [mg/mol]

#### X.c.3. Third Line

Column	Variable	Туре	Comment
1-10	KDEC(1)	REAL	(1)
11-20	KDEC(2)	REAL	(2)
21-30	KDEC(3)	REAL	(3)
31-40	KDEC(4)	REAL	(4)

- (1) Decay rates of biomass 1 [1/s]
- (2) Decay rates of biomass 2 [1/s]
- (3) *Decay rates of biomass 3* [1/s]
- (4) *Decay rates of biomass 4* [1/s]

### X.c.4. Fourth Line

Column	Variable	Туре	Comment
1-10	KM(1)	REAL	(1)
11-20	KM(2)	REAL	(2)

21-30	KM(3)	REAL	(3)
31-40	KM(4)	REAL	(4)
41-50	KM(5)	REAL	(5)

- (1) *Monod coefficient of electron acceptor* [mol/L]
- (2) *Monod coefficient PCE* [mol/L]
- (3) *Monod coefficient TCE* [mol/L]
- (4) *Monod coefficient DCE* [mol/L]
- (5) *Monod coefficient VC* [mol/L]

# X.c.5. Fifth Line

Column	Variable	Туре	Comment
1-10	ALPHAS	REAL	(1)
11-20	KAAB	REAL	(2)

(1) *Mass transfer coefficient* [1/s]

- (2) *First order decay describing competitive consumption of electron donor* [1/s]
- d) CHEMART = 4

Two-domain approach + aerobic degradation, sorption at equilibrium.

## X.d.1. First Line

Column	Variable	Туре	Comment
1-10	NIMM	REAL	Ratio of immobile to total porosity [-]
11-20	ALPHAS	REAL	Mass transfer coefficient [1/s]

# X.d.2. Second Line

Column	Variable	Туре	Comment
1-10	MUEMAX	REAL	(1)
11-20	YIELDS	REAL	(2)
21-30	YIELDO	REAL	(3)
31-40	KS	REAL	(4)
41-50	KO	REAL	(5)
51-60	KSTERB	REAL	(6)

(1) *Maximum growth rate* [1/s]

(2) *Yield coefficient of substrate* [mg/mg]

(3) *Yield coefficient of oxygen* [mg/mg]

(4) MONOD *coefficient of substrate* [mg/L]

(5) MONOD *coefficient of oxygen* [mg/L]

(6) *Decay rate of biomass* [1/s]

# A.2 CONTRACT-2 and CONTRACT-3

# I. Header

Column	Variable	Туре	Comment
1-80	UEB	CHARACTER*80	Header;
			appears in all output files

# II. Main Control Lines

# II.1. First Main Control Line

Column	Variable	Туре	Comment
1-5	CEMART	INTEGER	Type of chemistry model
6-10	ANZMOB	INTEGER	Number of mobile components
11-15	ANZIMM	INTEGER	Number of immobile components
16-20	ANZX	INTEGER	Number of cells in x direction
21-25	ANZY	INTEGER	Number of cells in y direction
26-30	ANZZK	INTEGER	Number of time curves

# II.2. Second Main Control Line

These parameters are used only for CONTRACT-2 (direct coupling). For CONTRACT-3 (operator-split coupling) use any parameters.

Column	Variable	Туре	Comment
1-5	KMP	INTEGER	(1)
6-10	MAXL	INTEGER	(2)
11-15	NRMNL	INTEGER	(3)
16-25	EPLI	REAL	(4)
26-30	NSAVE	INTEGER	(5)
31-35	ITMAX	INTER	(6)
36-40	LJAC	INTEGER	(7)

- (1) Order of KRYLOV subspace for GMRES solver used for nonlinear solver (DASPK)
- (2) Maximum number of iterations (DASPK)
- (3) Maximum number of restarts of the GMRES solver per nonlinear iteration (DASPK)
- (4) Convergence criterion of the GMRES solver (DASPK)

146		APPENDI	X A. DESCRIPTION OF INPUT FILES	
(5)	Order of KRYLOV subspa used for preconditioning	ce for GMRES solver		
(6)	Maximum number of iterations for GMRES-solver used for preconditioning			
(7)	Number of non-zero entries in the JACOBIAN			
II.3.	Third Main Control Lin	es		
Column	Variable	Туре	Comment	
1-10	TANF	REAL	Starting time [s]	
11-20	DTFL	REAL	Size of time steps for flow calculation [s]	
21-30	DTOUT	REAL	<i>Size of time steps for output protocol</i> [s]	
31-40	TEND	REAL	<i>End time</i> [s]	

# III. Time Curves

These lines are skipped for ANZZK=0. Each time curve requires at least two lines. Time curves are described by polygons. Values between two points in the time curve are evaluated by linear interpolation.

# III.1. Line 1

Column 1-5	Variable IPKT	Type INTEGER	Comment (1)
(1)	Number of points descri	bing the time curve	
III.2.	Line 2		
Column	Variable	Туре	Comment
1-10	ZEIT()	REAL	<i>Time value of the point</i> [s]
11-20	WERT()	REAL	Factor of the point

Line III.2. must be repeated IPKT times.

# IV. Spatial Discretization

# IV.1 x Direction

Column	Variable	Type	Comment (1)
1-10	DELTA-X(1)	REAL	
11-20	DELTA-X(2)	REAL	
 61-70	DELTA-X(7)	REAL	

#### A.2. CONTRACT-2 AND CONTRACT-3

(1) Each line contains 7 entries. INT(ANZX/7)+1 lines are required. The last line contains (ANZX MOD 7) entries. [m]

## IV.1 y Direction

61-70

Column	Variable	Туре	Comment
1-10	DELTA-Y(1)	REAL	(1)
11-20	DELTA-Y(2)	REAL	
•••••			

(1) Each line contains 7 entries. INT(ANZY/7)+1 lines are required. The last line contains (ANZY MOD 7) entries. [m]

REAL

# V. Soil Properties

DELTA-Y(7)

#### V.1. Number of Data Sets and Accuracy

ariable	Туре	Comment
NZMAT	INTEGER	(1)
NZDI	INTEGER	Number of nodes with fixed head
NZNE	INTEGER	Number of nodes with fixed volume flux
RELEPS	REAL	Relative error in H
ABSEPS	REAL	Absolute error in H [m]
	uriable NZMAT NZDI NZNE RELEPS ABSEPS	triableTypeNZMATINTEGERNZDIINTEGERNZNEINTEGERRELEPSREALABSEPSREAL

(1) Number of different data sets of soil properties

#### V.2. Soil Properties per Data Set

The following block of two lines must be repeated for each data set of soil properties.

### V.2.1 First Line

Column	Variable	Туре	Comment
1-10	KFM	REAL	(1)
11-20	KFT	REAL	(2)
21-30	KFAN	REAL	(3)
31-40	S	REAL	(4)
41-50	NE	REAL	(5)

(1) *Hydraulic conductivity in principal direction* [m/s]

(2) *Hydraulic conductivity in transverse direction* [m/s]

(3) Angle between principal direction of hydraulic conductivity and x direction [°].

(4) *Storativity* [-]

(5) *Porosity* [-]

# V.2..2 Second Line

Column	Variable	Туре	Comment
1-10	DZ	REAL	Cell thickness [m]
11-20	AL	REAL	Longitudinal dispersivity [m]
21-30	AT	REAL	Transverse dispersivity [m]
31-40	CORG	REAL	(1)

# (1) Mass fraction of organic carbon in dry soil. [-]

# V.3. Definition of Data Set Number for Each Cell

Column	Variable	Туре	Comment
1-10	IMAT(1)	INTEGER	(1)
11-20	IMAT(2)	INTEGER	

- 99-100 IMAT(10) INTEGER
- (1) Each line contains 10 entries. INT(ANZX\*ANZY/10)+1 lines are required. The last line contains (ANZX\*ANZY MOD 10) entries.

# VI. Boundary Conditions for the Flow Calculation

# VI.1. Fixed Hydraulic Head (DIRICHLET Boundary Condition)

Column	Variable	Туре	Comment
1-5	CN	INTEGER	Cell number
6-10	TC	INTEGER	<i>Number of time curve</i> (1)
11-20	R	REAL	Value [m]

<sup>(1)</sup> The value R is multiplied by the factor of the time curve. The factor of the time curve is 1.0 for TC=0

# VI.2. Fixed Volumetric Flux (NEUMANN Boundary Condition)

Column	Variable	Туре	Comment
1-5	CN	INTEGER	Cell number
6-10	TC	INTEGER	<i>Number of time curve</i> (1)
11-20	R	REAL	<i>Factor</i> [m <sup>3</sup> /s]

(1) The value R is multiplied by the time curve factor. The time curve factor is 1.0 for TC=0

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# VII. Component Related Parameters

#### VII.1. Name and Accuracy of Each Component

Column	Variable	Туре	Comment
1-10	NAME	CHARACTER*10	Name of component
11-20	AMFEHL	REAL	Maximum absolute error
21-30	RMFEHL	REAL	Maxunum relative error
31-40	CDEF	REAL	Initial concentration
41-50	DM	REAL	Molecular diffusion coefficient
51-60	KOC	REAL	Partitioning coefficient Corg-Water

#### VII.2. Number of Initial and Boundary Conditions

Column	Variable	Туре	Comment
1-5	NR(I)	INTEGER	(1)
6-10	NQ(I)	INTEGER	(2)
11-15	NC(I)	INTEGER	(3)

(1) Number of cells with fixed concentration of compound I.

(2) *Number of cells with fixed input concentration of compound I.* 

(3) Number of cells with special initial conditions for compound I.

This line must be repeated ANZKOM times.

# VIII. DIRICHLET Boundary Conditions (Fixed Concentration)

The following line must be repeated NR(I) times for compound I. ANZKOM blocks are requested.

Variable	Туре	Comment
CN	INTEGER	Cell number
TC	INTEGER	Number of time-curve (1)
R	REAL	Value
	Variable CN TC R	VariableTypeCNINTEGERTCINTEGERRREAL

(1) The value R is multiplied by the time curve factor. The time curve factor is 1.0 for TC=0

# IX. Inflow Boundary Conditions

The following line must be repeated NQ(I) times for compound I. ANZKOM blocks are requested.

Column	Variable	Туре	Comment
1-5	CN	INTEGER	Cell number
6-10	TC	INTEGER	Number of time curve (1)
11-19	R	REAL	Value

(1) The value R is multiplied by the time curve factor. The time curve factor is 1.0 for TC=0

# X. Initial Conditions

The following line must be repeated NC(I) times for compound I. ANZKOM blocks are requested.

Column	Variable	Туре	Comment
1-5	CN	INTEGER	Cell
6-15	R	REAL	Value

# XI. Chemistry Related Parameters

For CHEMART=0 the following lines can be skipped.

a) CHEMART = 1

Aerobic degradation, sorption at equilibrium.

Column	Variable	Туре	Comment
1-10	MUEMAX	REAL	(1)
11-20	YIELDS	REAL	(2)
21-30	YIELDO	REAL	(3)
31-40	KS	REAL	(4)
41-50	KO	REAL	(5)
51-60	KSTERB	REAL	(6)

- (1) *Maximum growth rate* [1/s]
- (2) *Yield coefficient of substrate* [mg/mg]
- (3) *Yield coefficient of oxygen* [mg/mg]
- (4) MONOD coefficient of substrate [mg/L]
- (5) MONOD *coefficient of oxygen* [mg/L]
- (6) *Decay rate of biomass* [1/s]

a) CHEMART = 2

Two-domain approach - no chemical transfomations.

Column	Variable	Туре	Comment
1-10	NIMM	REAL	Ratio of immobile to total porosity [-]
11-20	ALPHAS	REAL	Mass transfer coefficient [1/s]

b) CHEMART = 3

Reductive dechlorination of Tetrachloroethene - kinetic sorption.

#### XI.c.1. First Line

Column	Variable	Туре	Comment
1-10	MUEMAX(1)	REAL	(1)
11-20	MUEMAX(2)	REAL	(2)
21-30	MUEMAX(3)	REAL	(3)
31-40	MUEMAX(4)	REAL	(4)

(1) *Maximum growth rate of biomass 1* [1/s]

(2) *Maximum growth rate of biomass* 2 [1/s]

(3) *Maximum growth rate of biomass 3* [1/s]

(4) *Maximum growth rate of biomass 4* [1/s]

#### XI.c.2. Second Line

Column	Variable	Туре	Comment
1-10	YIELD(1)	REAL	(1)
11-20	YIELD(2)	REAL	(2)
21-30	YIELD(3)	REAL	(3)
31-40	YIELD(4)	REAL	(4)

(1) Yield coefficient of biomass I	! [m	g/mol]
------------------------------------	------	--------

(2) *Yield coefficient of biomass 2* [mg/mol]

(3) *Yield coefficient of biomass 3* [mg/mol]

(4) *Yield coefficient of biomass 4* [mg/mol]

#### XI.c.3. Third Line

Column	Variable	Туре	Comment
1-10	KDEC(1)	REAL	(1)
11-20	KDEC(2)	REAL	(2)
21-30	KDEC(3)	REAL	(3)
31-40	KDEC(4)	REAL	(4)

(1)	Decay	rates oj	f biomass	<i>l</i> [1/s]
-----	-------	----------	-----------	----------------

- (2) *Decay rates of biomass* 2 [1/s]
- (3) Decay rates of biomass 3 [1/s]
- (4) *Decay rates of biomass 4* [1/s]

#### XI.c.4. Fourth Line

Column	Variable	Туре	Comment
1-10	KM(1)	REAL	(1)
11-20	KM(2)	REAL	(2)
21-30	KM(3)	REAL	(3)
31-40	KM(4)	REAL	(4)
41-50	KM(5)	REAL	(5)

- (1) *Monod coefficient of electron acceptor* [mol/L]
- (2) *Monod coefficient PCE* [mol/L]
- (3) *Monod coefficient TCE* [mol/L]
- (4) *Monod coefficient DCE* [mol/L]
- (5) *Monod coefficient VC* [mol/L]

# XI.c.5. Fifth Line

Column	Variable	Туре	Comment
1-10	ALPHAS	REAL	(1)
11-20	KAAB	REAL	(2)

- (1) *Mass transfer coefficient* [1/s]
- (2) *First order decay describing competitive consumption of electron donor* [1/s]
- d) CHEMART = 4

Two-domain approach + aerobic degradation, sorption at equilibrium.

### XI.d.1. First Line

Column	Variable	Туре	Comment
1-10	NIMM	REAL	Ratio of immobile to total porosity [-]
11-20	ALPHAS	REAL	Mass transfer coefficient [1/s]

# XI.d.2. Second Line

Variable	Туре	Comment
MUEMAX	REAL	(1)
YIELDS	REAL	(2)
YIELDO	REAL	(3)
KS	REAL	(4)
KO	REAL	(5)
KSTERB	REAL	(6)
	Variable MUEMAX YIELDS YIELDO KS KO KSTERB	VariableTypeMUEMAXREALYIELDSREALYIELDOREALKSREALKOREALKSTERBREAL

- (1) *Maximum growth rate* [1/s]
- (2) *Yield coefficient of substrate* [mg/mg]
- (3) *Yield coefficient of oxygen* [mg/mg]
- (4) MONOD coefficient of substrate [mg/L]
- (5) MONOD coefficient of oxygen [mg/L]
- (6) *Decay rate of biomass* [1/s]

# **Appendix B**

# How to Extend the Reactive Model Systems

For the definition of the reactive sub-problem three subroutines must be provided: The subsroutine RES including the definition of the DAES, the subroutine JAC including the JACOBIAN of the DAES, and the subroutine CONSINI where time derivatives are initialized. Additionally the input routine CHEMREAD and the chemistry related common-block file chemcmn.inc may be changed.

A detailed definition of the routines RES and JAC is given in the source-code of DASSL. The following additional requirement must be met: The first ANZMOB equations are related to mobile compounds, the transport related terms are added by other routines. These equations should be ODE's.

In the following the definition of the reaction related subroutines are documented in their current state.

a	SUBROUTINE RES(T,Y	, YPRIME, CJ, DELTA, IRES, RPAR, IPAR)
C===== Ca C	Mnemonic :	FUNCTION FOR DDASSL
Cb C	Topic :	DEFINITION OF DAES RELATED TO REACTIVE PROCESSES
Cd C	Programmer :	O. CIRPKA
Cf	Parameter(s) :	
C<->R	т :	TIME
C<->R	ү :	CONCENTRATIONS
C<->R	YPRIME :	TIME DERIVATIVES OF Y
C<- R	DELTA :	RESIDUE
C < ->I	IRES :	INTEGER-FLAG
C ->R	RPAR :	REAL PARAMETER FIELD (DUMMY)
C ->I	IPAR :	INTEGER PARAMETER FIELD (DUMMY)
С		
Ch	Commons :	
С		FOR AEROBIC DEGRADATION (CHEMART=1)
С	I KD :	PARTITIONING COEFFICIENT FOR SUBSTRATE
С	I YIELDS :	YIELD COEFFICIENT FOR SUBSTRATE

С	I YIELDO :	YIELD COEFFICIENT FOR OXYGEN
С	I MUEMAX :	MAXIMUM GROWTH RATE
С	I KS :	MONOD-COEFFICIENT FOR SUBSTRATE
С	I КО :	MONOD-COEFFICIENT FOR OXYGEN
С		FOR TWO-DOMAIN APPROACH (CHEMART=2)
С	I ALPHAS :	MASS TRANSFER COEFF. IMM. <-> MOB.
С	I KD :	PARTITIONING COEFFICIENT
С		FOR REDUCTIVE DECHLORINATION (CHEMART=3)
С	I MUE1 :	MAXIMUM GROWTH RATE FOR BIOMASS 1
С	I MUE2 :	MAXIMUM GROWTH RATE FOR BIOMASS 2
С	I MUE3 :	MAXIMUM GROWTH RATE FOR BIOMASS 3
С	I MUE4 :	MAXIMUM GROWTH RATE FOR BIOMASS 4
С	I YIE1 :	YIELD COEFFICIENT FOR STEP 1
С	I YIE2 :	YIELD COEFFICIENT FOR STEP 2
С	I YIE3 :	YIELD COEFFICIENT FOR STEP 3
С	I YIE4 :	YIELD COEFFICIENT FOR STEP 4
С	I KD1 :	PARTITIONING COEFFICIENT FOR ELECTRON DONOR
С	I KD2 :	PARTITIONING COEFFICIENT FOR PCE
С	I KD3 :	PARTITIONING COEFFICIENT FOR TCE
С	I KD4 :	PARTITIONING COEFFICIENT FOR DCE
С	I KD5 :	PARTITIONING COEFFICIENT FOR VC
С	I KD6 :	PARTITIONING COEFFICIENT FOR ETHENE
С	I K1 :	MONOD-COEFFICIENT FOR ELECTRON DONOR
С	I K2 :	MONOD-COEFFICIENT FOR PCE
С	I КЗ :	MONOD-COEFFICIENT FOR TCE
С	I K4 :	MONOD-COEFFICIENT FOR DCE
С	I K5 :	MONOD-COEFFICIENT FOR VC
С	I K6 :	MONOD-COEFFICIENT FOR ETHENE
С	I ALPHAS :	MASS TRANSFER COEFF. DISS. <-> SORB.
Cz3456	5======================================	
	INCLUDE 'common.in	C ′
	INCLUDE 'chemcmn.in	nc'
	INTEGER*4 IRES, IPA	R
	REAL*8 T,Y(1:ANZKO	M), YPRIME(1:ANZKOM), DELTA(1:ANZKOM), RPAR, CJ
C	AEROBIC DEGRADATIO	N SORPTION AT EQUILIBRIUM
C	Y(1): SUBSTRATE DIS	SSOLVED
C	Y(2): OXYGEN DISSO	
C	Y(3): SUBSTRATE SO	RED
C	Y(4): BIOMASS	
	IF (CHEMART.EQ.I)	
	DELTA(1) = -MUEMAX	/YIELDS*Y(1)/(Y(1)+KS)*Y(2)/(Y(2)+KO)*Y(4)
	+ - YPRIME(1) - YPRIMI	
	DETIA(Z) = -MUEMAX	/YIELDU^Y(I)/(Y(I)+KS)*Y(Z)/(Y(Z)+KO)*Y(4)
	+ -YPKIME(2)	xr / つ )
	DELTA(3) = KD*Y(1)	-Y(3)
	DELTA(4) = (MUEMAX)	(1)/(1)+KS)(2)/(1(2)+KO)-KSTERB)*1(4)
	+ -YPRIME(4)	

С Y(1): MOBILE COMPONENT С Y(2): IMMOBILE COMPONENT ELSE IF (CHEMART.EQ.2) THEN DELTA(1) = -YPRIME(1) + ALPHAS\*(Y(2)/KD-Y(1))DELTA(2) = -YPRIME(2) + ALPHAS\*(Y(1) - Y(2)/KD)С PCE-DECHLORINATION AND KINETIC SORPTION С TWO ELCTRONS TRANSFERED PER ELECTRON DONOR С Y(1): E-DONOR DISSOLVED С Y(2): PCE DISSOLVED С Y(3): TCE DISSOLVED С Y(4): DCE DISSOLVED С Y(5): VC DISSOLVED С Y(6): ETHENE DISSOLVED С Y(7): E-DONOR SORBED С Y(8): PCE SORBED С Y(9): TCE SORBED С Y(10): DCE SORBED С Y(11): VC SORBED С Y(12): ETHENE SORBED С Y(13): BIOMASS 1 С Y(14): BIOMASS 2 С Y(15): BIOMASS 3 С Y(16): BIOMASS 4 ELSE IF (CHEMART.EQ.3) THEN DELTA(1) = -YPRIME(1) - KABB\*Y(1)-MUE1/YIE1\*Y(1)/(Y(1)+K1)\*Y(2)/(Y(2)+K2)\*Y(13) + -MUE2/YIE2\*Y(1)/(Y(1)+K1)\*Y(3)/(Y(3)+K3)\*Y(14) + -MUE3/YIE3\*Y(1)/(Y(1)+K1)\*Y(4)/(Y(4)+K4)\*Y(15) + -MUE4/YIE4\*Y(1)/(Y(1)+K1)\*Y(5)/(Y(5)+K5)\*Y(16) + +ALPHAS\*(Y(7)/KD1-Y(1))+ DELTA(2) = -YPRIME(2)-MUE1/YIE1\*Y(1)/(Y(1)+K1)\*Y(2)/(Y(2)+K2)\*Y(13) + +ALPHAS\*(Y(8)/KD2-Y(2)) + DELTA(3) = -YPRIME(3)+MUE1/YIE1\*Y(1)/(Y(1)+K1)\*Y(2)/(Y(2)+K2)\*Y(13) + -MUE2/YIE2\*Y(1)/(Y(1)+K1)\*Y(3)/(Y(3)+K3)\*Y(14) + +ALPHAS\*(Y(9)/KD3-Y(3))+ DELTA(4) = -YPRIME(4)+MUE2/YIE2\*Y(1)/(Y(1)+K1)\*Y(3)/(Y(3)+K3)\*Y(14) + -MUE3/YIE3\*Y(1)/(Y(1)+K1)\*Y(4)/(Y(4)+K4)\*Y(15) + +ALPHAS\*(Y(10)/KD4-Y(4))+ DELTA(5) = -YPRIME(5)+MUE3/YIE3\*Y(1)/(Y(1)+K1)\*Y(4)/(Y(4)+K4)\*Y(15) + -MUE4/YIE4\*Y(1)/(Y(1)+K1)\*Y(5)/(Y(5)+K5)\*Y(16) +

```
+ +ALPHAS*(Y(11)/KD5-Y(5))
```

```
DELTA(6) = -YPRIME(6)
+
      +MUE4/YIE4*Y(1)/(Y(1)+K1)*Y(5)/(Y(5)+K5)*Y(16)
      +ALPHAS*(Y(12)/KD6-Y(6))
+
     DELTA(7) = -YPRIME(7) + ALPHAS*(Y(1)-Y(7)/KD1)
     DELTA(8) = -YPRIME(8) + ALPHAS*(Y(2)-Y(8)/KD2)
     DELTA(9) = -YPRIME(9) + ALPHAS*(Y(3)-Y(9)/KD3)
     DELTA(10) = -YPRIME(10) + ALPHAS*(Y(4)-Y(10)/KD4)
     DELTA(11) = -YPRIME(11) + ALPHAS*(Y(5)-Y(11)/KD5)
     DELTA(12) = -YPRIME(12) + ALPHAS*(Y(6)-Y(12)/KD6)
     DELTA(13) = -YPRIME(13) - KSTERB1*Y(13)
      +MUE1*Y(1)/(Y(1)+K1)*Y(2)/(Y(2)+K2)*Y(13)
+
     DELTA(14) = -YPRIME(14) - KSTERB2*Y(14)
      +MUE2*Y(1)/(Y(1)+K1)*Y(3)/(Y(3)+K3)*Y(14)
+
     DELTA(15) = -YPRIME(15) - KSTERB3*Y(15)
      +MUE3*Y(1)/(Y(1)+K1)*Y(4)/(Y(4)+K4)*Y(15)
+
     DELTA(16) = -YPRIME(16) - KSTERB4*Y(16)
      +MUE4*Y(1)/(Y(1)+K1)*Y(5)/(Y(5)+K5)*Y(16)
+
С
     AEROBIC DEGRADATION PLUS TWO-DOMAIN APPROACH
С
     Y(1): SUBSTRATE MOBILE
С
     Y(2): OXYGEN MOBILE
С
     Y(3): SUBSTRATE IMMOBILE
С
     Y(4): OXYGEN IMMOBILE
С
     Y(5): SUBSTRATE SORBED MOBILE
С
     Y(6): SUBSTRATE SORBED IMMOBILE
С
     Y(7): BIOMASS MOBILE
С
     Y(8): BIOMASS IMMOBILE
      ELSE IF (CHEMART.EQ.4) THEN
     DELTA(1) = -MUEMAX/YIELDS*Y(1)/(Y(1)+KS)*Y(2)/(Y(2)+KO)*Y(7)
     +ALPHAS*(Y(3)-Y(1))
+
      -YPRIME(1)-YPRIME(5)
+
     DELTA(2) = -MUEMAX/YIELDO*Y(1)/(Y(1)+KS)*Y(2)/(Y(2)+KO)*Y(7)
      +ALPHAS*(Y(4)-Y(2))
+
      -YPRIME(2)
+
     DELTA(3) = -MUEMAX/YIELDS*Y(3)/(Y(3)+KS)*Y(4)/(Y(4)+KO)*Y(8)
      -(1.D0-NIMM)/NIMM*ALPHAS*(Y(3)-Y(1))
      -YPRIME(3)-YPRIME(6)
+
     DELTA(4) = -MUEMAX/YIELDO*Y(3)/(Y(3)+KS)*Y(4)/(Y(4)+KO)*Y(8)
      -(1.D0-NIMM)/NIMM*ALPHAS*(Y(4)-Y(2))
+
      -YPRIME(4)
+
```

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```
DELTA(5) = KD*Y(1)-Y(5)
DELTA(6) = KD*Y(3)-Y(6)
DELTA(7) = (MUEMAX*Y(1)/(Y(1)+KS)*Y(2)/(Y(2)+KO)-KSTERB)*Y(7)
+ -YPRIME(7)
DELTA(8) = (MUEMAX*Y(3)/(Y(3)+KS)*Y(4)/(Y(4)+KO)-KSTERB)*Y(8)
+ -YPRIME(8)
```

ENDIF RETURN END

```
SUBROUTINE JAC(T,Y,YPRIME,PD,CJ,RPAR,IPAR)
С
     _____
Ca
                    DEFENITION OF THE JACOBIAN FOR DDASSL
    Mnemonic :
    _____
С
Cb
    Topic :
                    ANALYTICAL CALCULATION OF JACONIAN
С
                    FOR REACTIVE PROCESSES
С
     _____
Cd
    Programmer :
                    O. CIRPKA 9/93
C
     _____
Cf Parameter(s) :
С<->R Т :
                    TIME
C<->R Y :
                    CONCENTRATIONS
C<->R YPRIME :
                    TIME DERIVATIVES OF Y
C<->I IRES :
                    INTEGER-FLAG
C \rightarrow R RPAR :
                   REAL PARAMETER FIELD (DUMMY)
C ->I IPAR :
                    INTEGER PARAMETER FIELD (DUMMY)
C<-> R PD :
                    JAKOBIMATRIX
C -> R CJ :
                    WICHTUNG DER ZEITABLEITUNG
С
    _____
Ch
    Commons :
                    FOR AEROBIC DEGRADATION (CHEMART=1)
С
С
                    PARTITIONING COEFFICIENT FOR SUBSTRATE
    I KD :
С
    I YIELDS :
                    YIELD COEFFICIENT FOR SUBSTRATE
С
    I YIELDO :
                    YIELD COEFFICIENT FOR OXYGEN
С
    I MUEMAX :
                    MAXIMUM GROWTH RATE
С
    I KS :
                    MONOD-COEFFICIENT FOR SUBSTRATE
С
                    MONOD-COEFFICIENT FOR OXYGEN
    I КО :
С
                    FOR TWO-DOMAIN APPROACH (CHEMART=2)
С
    I ALPHAS :
                    MASS TRANSFER COEFF. IMM. <-> MOB.
С
                    PARTITIONING COEFFICIENT
    I KD :
С
                    FOR REDUCTIVE DECHLORINATION (CHEMART=3)
С
    I MUE1 :
                    MAXIMUM GROWTH RATE FOR BIOMASS 1
С
    I MUE2 :
                    MAXIMUM GROWTH RATE FOR BIOMASS 2
С
    I MUE3 :
                    MAXIMUM GROWTH RATE FOR BIOMASS 3
С
    I MUE4 :
                    MAXIMUM GROWTH RATE FOR BIOMASS 4
С
    I YIEl :
                    YIELD COEFFICIENT FOR STEP 1
С
    I YIE2 :
                    YIELD COEFFICIENT FOR STEP 2
С
    I YIE3 :
                    YIELD COEFFICIENT FOR STEP 3
С
     I YIE4 :
                    YIELD COEFFICIENT FOR STEP 4
```

С	I KD1 :	PARTITIONING COEFFICIENT FOR ELECTRON DONOR
С	I KD2 :	PARTITIONING COEFFICIENT FOR PCE
С	I KD3 :	PARTITIONING COEFFICIENT FOR TCE
С	I KD4 :	PARTITIONING COEFFICIENT FOR DCE
С	I KD5 :	PARTITIONING COEFFICIENT FOR VC
С	I KD6 :	PARTITIONING COEFFICIENT FOR ETHENE
С	I K1 :	MONOD-COEFFICIENT FOR ELECTRON DONOR
С	I K2 :	MONOD-COEFFICIENT FOR PCE
С	I K3 :	MONOD-COEFFICIENT FOR TCE
С	I K4 :	MONOD-COEFFICIENT FOR DCE
С	I K5 :	MONOD-COEFFICIENT FOR VC
C	I K6 :	MONOD-COEFFICIENT FOR ETHENE
C	T ALPHAS :	MASS TRANSFER COEFF DISS <-> SORB
$C_{7}345$	 6===============================	
02313	INCLUDE (common in	c'
	INCLUDE 'chemann i	nc'
	INTEGER*4 IDAR	110
	DENI'8 T V(1·NN7KO	M) VDDIME(1· $\lambda$ NIZKOM) DD(1· $\lambda$ NIZKOM 1· $\lambda$ NIZKOM)
<u>т</u>	CI DDAD	$M_{j}, \text{IERIME}(1:\text{ANZROM}), \text{ED}(1:\text{ANZROM}, 1:\text{ANZROM}),$
т	CU, RPAR	
C		N CODUTION AT FOILT TODILIM
d	X(1). CUDCTDATE DI	SCOLVED
d	V(2): OVVCEN DISCO	
d	I(2). OXIGEN DISSO	
C a	Y(4): DIOMAG	KBLD
C	Y(4). BIOMASS	
a	IF (CHEMARI.EQ.I)	IHEN
C	PARITAL DERIVATIVE	S FOR SUBSTRATE
	PD(1,1) = -MUEMAX/Y1	ELDS*KS/(Y(1)+KS)/(Y(1)+KS)*
+	Y(2)/(Y(2)+KO)*Y(4)	$) = C_{\rm U}$
	PD(1,2) = -MUEMAX/YI	ELDS*Y(1)/(Y(1)+KS)*
+	KO/(Y(2)+KO)/(Y(2)	+KO)*Y(4)
	PD(1,3) = -CJ	
	PD(1,4) = -MUEMAX/YI	ELDS*Y(1)/(Y(1)+KS)*Y(2)/(Y(2)+KO)
С	PARTIAL DERIVATIVE	S FOR OXYGEN
	PD(2,1)=-MUEMAX/YI	ELDO*KS/(Y(1)+KS)/(Y(1)+KS)*
+	Y(2)/(Y(2)+KO)*Y(4	)
	PD(2,2) = -MUEMAX/YI	ELDO*Y(1)/(Y(1)+KS)*
+	KO/(Y(2)+KO)/(Y(2)	+KO)*Y(4) - CJ
	PD(2, 4) = -MUEMAX/YI	ELDO*Y(1)/(Y(1)+KS)*Y(2)/(Y(2)+KO)
С	PARTIAL DERIVATIVE	S FOR SORBED SUBSTRATE
	PD(3,1) = KD	
	PD(3,3) = -1.D0	
С	PARTIAL DERIVATIVE	S FOR BIOMASS
	PD(4,1)=MUEMAX*KS/	(Y(1)+KS)/(Y(1)+KS)*Y(2)/(Y(2)+KO)*Y(4)
	PD(4,2)=MUEMAX*Y(1	)/(Y(2)+KS)*KO/(Y(2)+KO)/(Y(2)+KO)*Y(4)
	PD(4,4)=MUEMAX*Y(1	)/(Y(1)+KS)*Y(2)/(Y(2)+KO)-KSTERB-CJ

- C Y(1): MOBILE COMPONENT
- C Y(2): IMMOBILE COMPONENT ELSE IF (CHEMART.EQ.2) THEN
- C PARTIAL DERIVATIVES FOR MOBILE COMPONENT PD(1,1)= -ALPHAS -CJ PD(1,2)= ALPHAS/KD
- C PARTIAL DERIVATIVES FOR IMMOBILE COMPONENT PD(2,1) = ALPHAS PD(2,2) = -ALPHAS/KD -CJ
- С PCE-DECHLORINATION AND KINETIC SORPTION С TWO ELCTRONS TRANSFERED PER ELECTRON DONOR С Y(1): E-DONOR DISSOLVED С Y(2): PCE DISSOLVED С Y(3): TCE DISSOLVED С Y(4): DCE DISSOLVED С Y(5): VC DISSOLVED С Y(6): ETHENE DISSOLVED С Y(7): E-DONOR SORBED С Y(8): PCE SORBED С Y(9): TCE SORBED С Y(10): DCE SORBED С Y(11): VC SORBED С Y(12): ETHENE SORBED С Y(13): BIOMASS 1 С Y(14): BIOMASS 2 С Y(15): BIOMASS 3 С Y(16): BIOMASS 4 ELSE IF (CHEMART.EQ.3) THEN С PARTIAL DERIVATIVES FOR DISSOLVED ELECTRON DONOR PD(1,1) = -CJ - KABB - ALPHAS-MUE1/YIE1\*K1/(Y(1)+K1)/(Y(1)+K1)\*Y(2)/(Y(2)+K2)\*Y(13) + -MUE2/YIE2\*K1/(Y(1)+K1)/(Y(1)+K1)\*Y(3)/(Y(3)+K3)\*Y(14) + -MUE3/YIE3\*K1/(Y(1)+K1)/(Y(1)+K1)\*Y(4)/(Y(4)+K4)\*Y(15) + -MUE4/YIE4\*K1/(Y(1)+K1)/(Y(1)+K1)\*Y(5)/(Y(5)+K5)\*Y(16)+ PD(1,2) =-MUE1/YIE1\*Y(1)/(Y(1)+K1)\*K2/(Y(2)+K2)/(Y(2)+K2)\*Y(13) + PD(1,3) =
- + -MUE2/YIE2\*Y(1)/(Y(1)+K1)\*K3/(Y(3)+K3)/(Y(3)+K3)\*Y(14) PD(1,4) =
- + -MUE3/YIE3\*Y(1)/(Y(1)+K1)\*K4/(Y(4)+K4)/(Y(4)+K4)\*Y(15) PD(1,5) =

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+ -MUE4/YIE4*Y(1)/(Y(1)+K1)*K5/(Y(5)+K5)/(Y(5)+K5)*Y(16)
PD(1,7) = +ALPHAS/KD1
PD(1,13)= -MUE1/YIE1*Y(1)/(Y(1)+K1)*Y(2)/(Y(2)+K2)
PD(1,14)= -MUE2/YIE2*Y(1)/(Y(1)+K1)*Y(3)/(Y(3)+K3)
PD(1,15)= -MUE3/YIE3*Y(1)/(Y(1)+K1)*Y(4)/(Y(4)+K4)
PD(1,16)= -MUE4/YIE4*Y(1)/(Y(1)+K1)*Y(5)/(Y(5)+K5)
```

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С
      PARTIAL DERIVATIVES FOR DISSOLVED PCE
      PD(2,1) = -MUE1/YIE1*K1/(Y(1)+K1)/(Y(1)+K1)*Y(2)/(Y(2)+K2)*Y(13)
      PD(2,2) = -MUE1/YIE1*Y(1)/(Y(1)+K1)*K2/(Y(2)+K2)/(Y(2)+K2)*Y(13)
      -ALPHAS - CJ
+
      PD(2,8) = ALPHAS/KD2
      PD(2,13) = -MUE1/YIE1*Y(1)/(Y(1)+K1)*Y(2)/(Y(2)+K2)
С
      PARTIAL DERIVATIVES FOR DISSOLVED TCE
      PD(3,1) = +MUE1/YIE1*K1/(Y(1)+K1)/(Y(1)+K1)*Y(2)/(Y(2)+K2)*Y(13)
      -MUE2/YIE2*K1/(Y(1)+K1)/(Y(1)+K1)*Y(3)/(Y(3)+K3)*Y(14)
+
      PD(3,2) = +MUE1/YIE1*Y(1)/(Y(1)+K1)*K2/(Y(2)+K2)/(Y(2)+K2)*Y(13))
      PD(3,3) = -MUE2/YIE2*Y(1)/(Y(1)+K1)*K3/(Y(3)+K3)/(Y(3)+K3)*Y(14)
      -ALPHAS -CJ
+
      PD(3,9) = ALPHAS/KD3
      PD(3,13) = +MUE1/YIE1*Y(1)/(Y(1)+K1)*Y(2)/(Y(2)+K2)
      PD(3,14) = -MUE2/YIE2*Y(1)/(Y(1)+K1)*Y(3)/(Y(3)+K3)
С
      PARTIAL DERIVATIVES FOR DISSOLVED DCE
      PD(4,1) = +MUE2/YIE2*K1/(Y(1)+K1)/(Y(1)+K1)*Y(3)/(Y(3)+K3)*Y(14)
      -MUE3/YIE3*K1/(Y(1)+K1)/(Y(1)+K1)*Y(4)/(Y(4)+K4)*Y(15)
+
      PD(4,3) = +MUE2/YIE2*Y(1)/(Y(1)+K1)*K3/(Y(3)+K3)/(Y(3)+K3)*Y(14)
      PD(4,4) = -MUE3/YIE3*Y(1)/(Y(1)+K1)*K4/(Y(4)+K4)/(Y(4)+K4)*Y(15))
+
      -ALPHAS -CJ
      PD(4,10) = ALPHAS/KD4
      PD(4,14) = +MUE2/YIE2*Y(1)/(Y(1)+K1)*Y(3)/(Y(3)+K3)
      PD(4,15) = -MUE3/YIE3*Y(1)/(Y(1)+K1)*Y(4)/(Y(4)+K4)
С
      PARTIAL DERIVATIVES FOR DISSOLVED VC
      PD(5,1) = +MUE3/YIE3*K1/(Y(1)+K1)/(Y(1)+K1)*Y(4)/(Y(4)+K4)*Y(15)
      -MUE4/YIE4*K1/(Y(1)+K1)/(Y(1)+K1)*Y(5)/(Y(5)+K5)*Y(16)
+
      PD(5,4) = +MUE3/YIE3*Y(1)/(Y(1)+K1)*K4/(Y(4)+K4)/(Y(4)+K4)*Y(15))
      PD(5,5) = -MUE4/YIE4*Y(1)/(Y(1)+K1)*K5/(Y(5)+K5)/(Y(5)+K5)*Y(16))
      -ALPHAS -CJ
+
      PD(5,11) = ALPHAS/KD5
      PD(5,15) = +MUE3/YIE3*Y(1)/(Y(1)+K1)*Y(4)/(Y(4)+K4)
      PD(5,16) = -MUE4/YIE4*Y(1)/(Y(1)+K1)*Y(5)/(Y(5)+K5)
С
      PARTIAL DERIVATIVES FOR DISSOLVED ETHENE
      PD(6,1) = +MUE4/YIE4*K1/(Y(1)+K1)/(Y(1)+K1)*Y(5)/(Y(5)+K5)*Y(16)
      PD(6,5) = +MUE4/YIE4*Y(1)/(Y(1)+K1)*K5/(Y(5)+K5)/(Y(5)+K5)*Y(16))
      PD(6,6) = -ALPHAS -CJ
      PD(6, 12) = ALPHAS/KD6
      PD(6,16) = +MUE4/YIE4*Y(1)/(Y(1)+K1)*Y(5)/(Y(5)+K5)
С
      PARTIAL DERIVATIVES FOR SORBED ELECTRON DONOR
      PD(7,1) = ALPHAS
      PD(7,7) = -CJ - ALPHAS/KD1
С
      PARTIAL DERIVATIVES FOR SORBED PCE
      PD(8,2) = ALPHAS
```

PD(8,8) = -CJ - ALPHAS/KD2

- C PARTIAL DERIVATIVES FOR SORBED TCE PD(9,3) = ALPHAS PD(9,9) = -CJ -ALPHAS/KD3
- C PARTIAL DERIVATIVES FOR SORBED DCE PD(10,4) = ALPHAS PD(10,10) = -CJ -ALPHAS/KD4
- C PARTIAL DERIVATIVES FOR SORBED VC PD(11,5) = ALPHAS PD(11,11)= -CJ -ALPHAS/KD5
- C PARTIAL DERIVATIVES FOR SORBED ETHENE PD(12,6) = ALPHAS PD(12,12)= -CJ -ALPHAS/KD6
- C PARTIAL DERIVATIVES FOR BIOMASS 1 PD(13,1) = +MUE1\*K1/(Y(1)+K1)/(Y(1)+K1)\*Y(2)/(Y(2)+K2)\*Y(13) PD(13,2) = +MUE1\*Y(1)/(Y(1)+K1)\*K2/(Y(2)+K2)/(Y(2)+K2)\*Y(13) PD(13,13)= -CJ -KSTERB1 +MUE1\*Y(1)/(Y(1)+K1)\*Y(2)/(Y(2)+K2)
- C PARTIAL DERIVATIVES FOR BIOMASS 2 PD(14,1) = +MUE2\*K1/(Y(1)+K1)/(Y(1)+K1)\*Y(3)/(Y(3)+K3)\*Y(14) PD(14,3) = +MUE2\*Y(1)/(Y(1)+K1)\*K3/(Y(3)+K3)/(Y(3)+K3)\*Y(14) PD(14,14)= -CJ -KSTERB2 +MUE2\*Y(1)/(Y(1)+K1)\*Y(3)/(Y(3)+K3)
- C PARTIAL DERIVATIVES FOR BIOMASS 3 PD(15,1) = +MUE3\*K1/(Y(1)+K1)/(Y(1)+K1)\*Y(4)/(Y(4)+K4)\*Y(15) PD(15,4) = +MUE3\*Y(1)/(Y(1)+K1)\*K4/(Y(4)+K4)/(Y(4)+K4)\*Y(15) PD(15,15)= -CJ -KSTERB3 +MUE3\*Y(1)/(Y(1)+K1)\*Y(4)/(Y(4)+K4)
- C PARTIAL DERIVATIVES BIOMASS 4
  PD(16,1) = +MUE4\*K1/(Y(1)+K1)/(Y(1)+K1)\*Y(5)/(Y(5)+K5)\*Y(16)
  PD(16,5) = +MUE4\*Y(1)/(Y(1)+K1)\*K5/(Y(5)+K5)/(Y(5)+K5)\*Y(16)
  PD(16,16)= -CJ -KSTERB4 +MUE4\*Y(1)/(Y(1)+K1)\*Y(5)/(Y(5)+K5)
- C AEROBIC DEGRADATION PLUS TWO-DOMAIN APPROACH
- C Y(1): SUBSTRATE MOBILE
- C Y(2): OXYGEN MOBILE
- C Y(3): SUBSTRATE IMMOBILE
- C Y(4): OXYGEN IMMOBILE
- C Y(5): SUBSTRATE SORBED MOBILE
- C Y(6): SUBSTRATE SORBED IMMOBILE
- C Y(7): BIOMASS MOBILE
- C Y(8): BIOMASS IMMOBILE
  - ELSE IF (CHEMART.EQ.4) THEN
- C PARTIAL DERIVATIVES FOR MOBILE SUBSTRATE PD(1,1)=-MUEMAX/YIELDS\*KS/(Y(1)+KS)/(Y(1)+KS)\*Y(2)/(Y(2)+KO)\*Y(7)

-ALPHAS - CJ + PD(1,2) = -MUEMAX/YIELDS\*Y(1)/(Y(1)+KS)\*KO/(Y(2)+KO)/(Y(2)+KO)\*Y(7)PD(1,3)=ALPHAS PD(1,5) = -CJPD(1,7) = -MUEMAX/YIELDS\*Y(1)/(Y(1)+KS)\*Y(2)/(Y(2)+KO)С PARTIAL DERIVATIVES FOR MOBILE OXYGEN PD(1,2) = -MUEMAX/YIELDO\*KS/(Y(1)+KS)/(Y(1)+KS)/(Y(2)+KO)\*Y(7)PD(2,2)=-MUEMAX/YIELDO\*Y(1)/(Y(1)+KS)\*KO/(Y(2)+KO)/(Y(2)+KO)\*Y(7) + -ALPHAS - CJ PD(2,4) = ALPHASPD(2,7) = -MUEMAX/YIELDO\*Y(1)/(Y(1)+KS)\*Y(2)/(Y(2)+KO)С PARTIAL DERIVATIVES FOR IMMOBILE SUBSTRATE PD(3,1) = (1.D0 - NIMM) / NIMM\*ALPHASPD(3,3) = -MUEMAX/YIELDS\*KS/(Y(3)+KS)/(Y(3)+KS)\*Y(4)/(Y(4)+KO)\*Y(8)+ -(1.D0-NIMM)/NIMM\*ALPHAS -CJ PD(3,4) = -MUEMAX/YIELDS\*Y(3)/(Y(3)+KS)\*KO/(Y(4)+KO)/(Y(4)+KO)\*Y(8)PD(3, 6) = -CJPD(3,8) = -MUEMAX/YIELDS\*Y(3)/(Y(3)+KS)\*Y(4)/(Y(4)+KO)С PARTIAL DERIVATIVES FOR IMMOBILE OXYGEN PD(4,2) = (1.D0 - NIMM) / NIMM\*ALPHASPD(4,3) = -MUEMAX/YIELDO\*KS/(Y(3)+KS)/(Y(3)+KS)\*Y(4)/(Y(4)+KO)\*Y(8)PD(4,4) = -MUEMAX/YIELDO\*Y(3)/(Y(3)+KS)\*KO/(Y(4)+KO)/(Y(4)+KO)\*Y(8)-(1.D0-NIMM)/NIMM\*ALPHAS -CJ + PD(4,8) = -MUEMAX/YIELDO\*Y(3)/(Y(3)+KS)\*Y(4)/(Y(4)+KO)С PARTIAL DERIVATIVES FOR MOBILE SUBSTRATE SORBED PD(5,1) = KDPD(5,5) = -1.D0С PARTIAL DERIVATIVES FOR IMMOBILE SUBSTRATE SORBED PD(6,3) = KDPD(6, 6) = -1.D0С PARTIAL DERIVATIVES FOR MOBILE BIOMASS PD(7,1) = MUEMAX\*KS/(Y(1)+KS)/(Y(1)+KS)\*Y(2)/(Y(2)+KO)\*Y(7)PD(7,2) = MUEMAX\*Y(1)/(Y(1)+KS)\*KO/(Y(2)+KO)/(Y(2)+KO)\*Y(7) PD(7,7) = MUEMAX\*Y(1)/(Y(1)+KS)\*Y(2)/(Y(2)+KO)-KSTERB - CJС PARTIAL DERIVATIVES FOR IMMOBILE BIOMASS PD(8,3) = MUEMAX\*KS/(Y(3)+KS)/(Y(3)+KS)\*Y(4)/(Y(4)+KO)\*Y(8)PD(8,4) = MUEMAX\*Y(3)/(Y(3)+KS)\*KO/(Y(4)+KO)/(Y(4)+KO)\*Y(8)PD(8,8) = MUEMAX\*Y(3)/(Y(3)+KS)\*Y(4)/(Y(4)+KO)-KSTERB - CJ ENDIF RETURN

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END

SUBROUTINE CONSINI(Y, YPRIME)

Mnemonic : CONSISTENT INITIAL CONDITION FOR DDASSL Ca С \_\_\_\_\_ Cb CONSISTENT INITIAL CONDITIONS FOR DAES Topic : С RELATED TO REACTIVE PROCESSES С \_\_\_\_\_ Cd Programmer : O. CIRPKA С Cf Parameter(s) : C<->R Y : CONCENTRATIONS C<->R YPRIME : TIME DERIVATIVES OF Y С \_\_\_\_\_ Ch Commons : С FOR AEROBIC DEGRADATION (CHEMART=1) С I KD : PARTITIONING COEFFICIENT FOR SUBSTRATE С I YIELDS : YIELD COEFFICIENT FOR SUBSTRATE С I YIELDO : YIELD COEFFICIENT FOR OXYGEN С I MUEMAX : MAXIMUM GROWTH RATE С I KS : MONOD-COEFFICIENT FOR SUBSTRATE С I КО : MONOD-COEFFICIENT FOR OXYGEN С FOR TWO-DOMAIN APPROACH (CHEMART=2) MASS TRANSFER COEFF. IMM. <-> MOB. С I ALPHAS : С I KD : PARTITIONING COEFFICIENT FOR REDUCTIVE DECHLORINATION (CHEMART=3) С С I MUEl : MAXIMUM GROWTH RATE FOR BIOMASS 1 С I MUE2 : MAXIMUM GROWTH RATE FOR BIOMASS 2 С I MUE3 : MAXIMUM GROWTH RATE FOR BIOMASS 3 С MAXIMUM GROWTH RATE FOR BIOMASS 4 I MUE4 : С I YIEl : YIELD COEFFICIENT FOR STEP 1 С I YIE2 : YIELD COEFFICIENT FOR STEP 2 С I YIE3 : YIELD COEFFICIENT FOR STEP 3 С I YIE4 : YIELD COEFFICIENT FOR STEP 4 С PARTITIONING COEFFICIENT FOR ELECTRON DONOR I KD1 : С I KD2 : PARTITIONING COEFFICIENT FOR PCE С I KD3 : PARTITIONING COEFFICIENT FOR TCE С PARTITIONING COEFFICIENT FOR DCE I KD4 : С I KD5 : PARTITIONING COEFFICIENT FOR VC С PARTITIONING COEFFICIENT FOR ETHENE I KD6 : С I K1 : MONOD-COEFFICIENT FOR ELECTRON DONOR С I K2 : MONOD-COEFFICIENT FOR PCE С I K3 : MONOD-COEFFICIENT FOR TCE С I K4 : MONOD-COEFFICIENT FOR DCE С I K5 : MONOD-COEFFICIENT FOR VC С I Кб : MONOD-COEFFICIENT FOR ETHENE С I ALPHAS : MASS TRANSFER COEFF. DISS. <-> SORB. С \_\_\_\_\_ Ch Local Variable : TOTAL MASS OF SUBSTRATE C R SGES : INCLUDE 'common.inc'

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INCLUDE 'chemcmn.inc'
      REAL*8 Y(1:ANZKOM), YPRIME(1:ANZKOM), SGES
С
      AEROBIC DEGRADATION SORPTION AT EQUILIBRIUM
С
      Y(1): SUBSTRATE DISSOLVED
С
      Y(2): OXYGEN DISSOLVED
С
      Y(3): SUBSTRATE SORBED
С
      Y(4): BIOMASS
      IF (CHEMART.EQ.1) THEN
С
      SORPTION EQUILIBRIUM
      SGES=Y(1)+Y(3)
      Y(1) = SGES / (1.D0 + KD)
      Y(3) = SGES - Y(1)
С
      TIME DERIVATIVES
      YPRIME(1) = (-MUEMAX/YIELDS*Y(1)/(Y(1)+KS)*Y(2)/(Y(2)+KO)*Y(4))
      /(1.D0+KD)
+
      YPRIME(2) = -MUEMAX/YIELDO*Y(1)/(Y(1)+KS)*Y(2)/(Y(2)+KO)*Y(4)
      YPRIME(3) = (-MUEMAX/YIELDS*Y(1)/(Y(1)+KS)*Y(2)/(Y(2)+KO)*Y(4))
      *KD/(1.D0+KD)
+
С
      YPRIME(3) = YPRIME(1) * KD
      YPRIME(4) = (MUEMAX*Y(1)/(Y(1)+KS)*Y(2)/(Y(2)+KO)-KSTERB)*Y(4)
С
      NO TRANSFORMATIONS TWO-DOMAIN APPROACH
С
      Y(1): MOBILE COMPONENT
С
      Y(2): IMMOBILE COMPONENT
      ELSE IF (CHEMART.EQ.2) THEN
      YPRIME(1) = ALPHAS*(Y(2)/KD-Y(1))
      YPRIME(2) = ALPHAS*(Y(1)-Y(2)/KD)
      PCE-DECHLORINATION AND KINETIC SORPTION
С
С
      TWO ELCTRONS TRANSFERED PER ELECTRON DONOR
С
      Y(1): E-DONOR DISSOLVED
С
      Y(2): PCE DISSOLVED
С
      Y(3): TCE DISSOLVED
С
      Y(4): DCE DISSOLVED
С
      Y(5): VC DISSOLVED
С
      Y(6): ETHENE DISSOLVED
С
      Y(7): E-DONOR SORBED
С
      Y(8): PCE SORBED
С
      Y(9): TCE SORBED
С
      Y(10): DCE SORBED
С
      Y(11): VC SORBED
С
      Y(12): ETHENE SORBED
С
      Y(13): BIOMASS 1
С
      Y(14): BIOMASS 2
С
      Y(15): BIOMASS 3
С
      Y(16): BIOMASS 4
      ELSE IF (CHEMART.EQ.3) THEN
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YPRIME(1) = - KABB*Y(1)
      -MUE1/YIE1*Y(1)/(Y(1)+K1)*Y(2)/(Y(2)+K2)*Y(13)
+
      -MUE2/YIE2*Y(1)/(Y(1)+K1)*Y(3)/(Y(3)+K3)*Y(14)
+
+
      -MUE3/YIE3*Y(1)/(Y(1)+K1)*Y(4)/(Y(4)+K4)*Y(15)
      -MUE4/YIE4*Y(1)/(Y(1)+K1)*Y(5)/(Y(5)+K5)*Y(16)
+
      +ALPHAS*(Y(7)/KD1-Y(1))
+
      YPRIME(2) =
      -MUE1/YIE1*Y(1)/(Y(1)+K1)*Y(2)/(Y(2)+K2)*Y(13)
+
+
      +ALPHAS*(Y(8)/KD2-Y(2))
      YPRIME(3) =
      +MUE1/YIE1*Y(1)/(Y(1)+K1)*Y(2)/(Y(2)+K2)*Y(13)
+
      -MUE2/YIE2*Y(1)/(Y(1)+K1)*Y(3)/(Y(3)+K3)*Y(14)
+
      +ALPHAS*(Y(9)/KD3-Y(3))
+
      YPRIME(4) =
      +MUE2/YIE2*Y(1)/(Y(1)+K1)*Y(3)/(Y(3)+K3)*Y(14)
+
      -MUE3/YIE3*Y(1)/(Y(1)+K1)*Y(4)/(Y(4)+K4)*Y(15)
+
      +ALPHAS*(Y(10)/KD4-Y(4))
+
      YPRIME(5) =
      +MUE3/YIE3*Y(1)/(Y(1)+K1)*Y(4)/(Y(4)+K4)*Y(15)
+
      -MUE4/YIE4*Y(1)/(Y(1)+K1)*Y(5)/(Y(5)+K5)*Y(16)
+
      +ALPHAS*(Y(11)/KD5-Y(5))
+
      YPRIME(6) =
      +MUE4/YIE4*Y(1)/(Y(1)+K1)*Y(5)/(Y(5)+K5)*Y(16)
+
      +ALPHAS*(Y(12)/KD6-Y(6))
+
      YPRIME(7) = ALPHAS*(Y(1)-Y(7)/KD1)
      YPRIME(8) = ALPHAS*(Y(2)-Y(8)/KD2)
      YPRIME(9) = ALPHAS*(Y(3)-Y(9)/KD3)
      YPRIME(10) = ALPHAS*(Y(4)-Y(10)/KD4)
      YPRIME(11) = ALPHAS*(Y(5)-Y(11)/KD5)
      YPRIME(12) = ALPHAS*(Y(6)-Y(12)/KD6)
      YPRIME(13) = - KSTERB1*Y(13)
      +MUE1*Y(1)/(Y(1)+K1)*Y(2)/(Y(2)+K2)*Y(13)
+
      YPRIME(14) = - KSTERB2*Y(14)
      +MUE2*Y(1)/(Y(1)+K1)*Y(3)/(Y(3)+K3)*Y(14)
+
      YPRIME(15) = - KSTERB3*Y(15)
      +MUE3*Y(1)/(Y(1)+K1)*Y(4)/(Y(4)+K4)*Y(15)
+
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YPRIME(16) = - KSTERB4*Y(16)
      +MUE4*Y(1)/(Y(1)+K1)*Y(5)/(Y(5)+K5)*Y(16)
+
С
      AEROBIC DEGRADATION PLUS TWO-DOMAIN APPROACH
С
      Y(1): SUBSTRATE MOBILE
С
      Y(2): OXYGEN MOBILE
С
      Y(3): SUBSTRATE IMMOBILE
С
      Y(4): OXYGEN IMMOBILE
С
      Y(5): SUBSTRATE SORBED MOBILE
С
      Y(6): SUBSTRATE SORBED IMMOBILE
С
      Y(7): BIOMASS MOBILE
С
      Y(8): BIOMASS IMMOBILE
      ELSE IF (CHEMART.EQ.4) THEN
      SGES=Y(1)+Y(5)
      Y(1) = SGES / (1.D0 + KD)
      Y(5) = SGES - Y(1)
      SGES=Y(3)+Y(6)
      Y(3) = SGES / (1.D0 + KD)
      Y(6) = SGES - Y(3)
      YPRIME(1) = (-MUEMAX/YIELDS*Y(1)/(Y(1)+KS)*Y(2)/(Y(2)+KO)*Y(7))
      +ALPHAS*(Y(3)-Y(1)))/(1.D0+KD)
+
      \text{YPRIME}(2) = -\text{MUEMAX}/\text{YIELDO*Y}(1)/(Y(1)+\text{KS})*Y(2)/(Y(2)+\text{KO})*Y(7)
      +ALPHAS*(Y(4)-Y(2))
+
      YPRIME(3) = (-MUEMAX/YIELDS*Y(3)/(Y(3)+KS)*Y(4)/(Y(4)+KO)*Y(8))
      -(1.D0-NIMM)/NIMM*ALPHAS*(Y(3)-Y(1)))/(1.D0+KD)
+
      YPRIME(4) = -MUEMAX/YIELDO*Y(3)/(Y(3)+KS)*Y(4)/(Y(4)+KO)*Y(8)
      -(1.D0-NIMM)/NIMM*ALPHAS*(Y(4)-Y(2))
+
      YPRIME(5) = (-MUEMAX/YIELDS*Y(1)/(Y(1)+KS)*Y(2)/(Y(2)+KO)*Y(7))
      +ALPHAS*(Y(3)-Y(1)))*KD/(1.D0+KD)
+
      YPRIME(6) = (-MUEMAX/YIELDS*Y(3)/(Y(3)+KS)*Y(4)/(Y(4)+KO)*Y(8))
+
      -(1.D0-NIMM)/NIMM*ALPHAS*(Y(3)-Y(1)))*KD/(1.D0+KD)
      YPRIME(7) = (MUEMAX*Y(1)/(Y(1)+KS)*Y(2)/(Y(2)+KO)-KSTERB)*Y(7)
      YPRIME(8) = (MUEMAX*Y(3)/(Y(3)+KS)*Y(4)/(Y(4)+KO)-KSTERB)*Y(8)
      ENDIF
      RETURN
      END
```

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# Appendix C

# Notation

Vectors are underlined, tensors are underlined twice.

# **Spatial derivatives**

$\nabla$	Gradient (note: gradient of a vector is a second order tensor)
$ abla_x$	Gradient in global coordinates
$ abla_s$	Gradient in local coordinates
$ abla \cdot ()$	Divergence of a vector

### Dimensions

L	Length
М	Mass
Т	Time

Variable	Physical Meaning	Dimension
<u>A</u>	Matrix of nodal coordinates	[L]
A	Mobility matrix (FEM)	$[L^3/T]$
$\overline{\alpha}$	Dispersivity (1D)	[L]
$\alpha_l$	Longitudinal dispersivity (2D/3D)	[L]
$\alpha_{sorb}$	Mass transfer coefficient of sorption	[1/T]
$\alpha_t$	Transverse dispersivity (2D/3D)	[L]
$\underline{AEC}$	Antidiffusive element contribution to a node (FCT, FEM)	[M/T]
c	Concentration	$[M/L^3]$
$\hat{c}$	Nodal concentrations	$[M/L^3]$
$c_A$	Electron acceptor concentration	$[M/L^3]$
$c^{\alpha}$	Conc. evaluated by weighting of upwind and central differentiation	$[M/L^3]$
$c^{cd}$	Concentration evaluated by central differentiation	$[M/L^3]$
$c_D$	Electron donor concentration	$[M/L^3]$
$C_{\frac{1}{2}}$	Half concentration of sorption (LANGMUIR isotherm)	$[M/L^3]$
$\tilde{c_{in}}$	Input concentration	$[M/L^3]$
$c_O$	Oxygen concentration	$[M/L^3]$

$c_P$	Concentration of primary carbon source	$[M/L^3]$
$c_S$	Substrate concentration	$[M/L^3]$
$c^*_{sorb}$	Concentration of sorbed compound related to pore volume	$[M/L^3]$
$c_{sorb}^{max}$	Maximum sorption capacity (LANGMUIR isotherm)	$[M/L^3]$
$c^{up}$	Upwind concentration	$[M/L^3]$
$c_w$	Concentration in water	$[M/L^3]$
$[CHC_i]$	Concentration of chlorinated hydrocarbon	$[M/L^3]$
Cr	COURANT number	[-]
<u>D</u>	Effective diffusion tensor	$[L^2/T]$
$\overline{D}_l$	Effective longitudinal diffusion coefficient	$[L^2/T]$
$D_m$	Molecular diffusion coefficient	$[L^2/T]$
$D_t$	Effective transverse diffusion coefficient	$[L^2/T]$
$\Delta t$	Size of time step	[T]
$\Delta x$	Grid spacing in x-direction	[L]
$\Delta y$	Grid spacing in y-direction	[L]
$\Delta z$	Grid spacing in z-direction	[L]
e	Truncation error (index indicates order)	$[M/T/L^3]$
ε	Residue (FEM)	$[M/T/L^3]$
$[E_{don}]$	Concentration of electron donor	$[M/L^3]$
$\phi$	Slope relative to central differentiation slope (slope limiter approach)	[-]
$\phi$	Weighting function (FEM)	[-]
$\overline{F}_{ad}$	Antidiffusive flux (FCT approach, FDM discretization)	[M/T]
foc	Organic carbon content of dry soil	$[M/L^3]$
$F_h$	High order flux (FCT approach, FDM discretization)	[M/T]
$F_l$	Low order flux (FCT approach, FDM discretization)	[M/T]
Γ	Boundary of the domain	$[L^2]$
h	Piezometric head	[L]
$\underline{HEC}$	High order element contribution to a node (FCT, FEM discretization)	[M/T]
<u>J</u>	JACOBIAN matrix	[L]
$\overline{J}_m$	Mass flux	$[M/L^2/T]$
K	Parameter of the FREUNDLICH isotherm	[-]
$K_d$	Partitioning coefficient sorbed $\leftrightarrow$ aqueous phase	[-]
$\underline{k}_{f}$	Hydraulic conductivity tensor	[L/T]
$\overline{\mathcal{L}}^{J}$	Differential operator	
$\mathcal{L}^*$	Adjoint differential operator	
$k_{dec}$	Decay rate	[1/T]
$k_{ar}$	Growth rate	[1/T]
$\vec{K_i}$	Inhibition concentration (MONOD-HALDANE kinetics)	$[M/L^3]$
$K_{inh}$	Inhibition concentration (general kinetics)	$[M/L^3]$
$K_m$	MICHAELIS-MENTEN or MONOD coefficient	$[M/L^3]$
$K_O$	MICHAELIS-MENTEN coefficient for oxygen	$[M/L^3]$
$K_{S}^{\circ}$	MICHAELIS-MENTEN coefficient for substrate	$[M/L^3]$
$k_{m\leftrightarrow i}$	Mass transfer coefficient mobile $\leftrightarrow$ immobile porosity	[1/T]
$K_{OC}$	Partitioning coefficient organic carbon $\leftrightarrow$ water	[-]
λ	First-order decay coefficient	[1/T]
LEC	Low-order element contribution to a node (FCT. FEM discretization)	[M/T]
$\overline{M}$	Mass matrix (FEM)	[L <sup>3</sup> ]
$\overline{\mu_{max}}$	Maximum growth rate	[1/T]

n	Parameter of the FREUNDLICH isotherm	[-]
<u>n</u>	Unit vector normal to surface	[-]
$n_e$	Effective porosity	[-]
$n_{imm}$	Immobile porosity	[-]
$n_{mob}$	Mobile porosity	[-]
ν	Iteration index	
Ne	NEUMANN number	[-]
$\underline{\Omega}$	Shape function	[-]
$\omega^C$	Corrector polynomial (multistep time integration)	
$\omega^P$	Predictor polynomial (multistep time integration)	
$P_{i,j}^{\pm}$	Sum of positive/negative antidiffusive fluxes (FCT approach)	[M/T]
$P\tilde{e}$	PECLET number	[-]
$Q_{i,j}^{\pm}$	Maximum/minimum allowable antidiffusive fluxes (FCT approach)	[M/T]
$q_{in,out}$	Volumetric source-sink term related to volume	[1/T]
r	Reaction rate	$[M/L^3/T]$
$\hat{r}$	Nodal reaction rates	$[M/L^3/T]$
ho	Soil density	$[M/L^3]$
ho	Convergence rate (multistep time integration)	
$R_{i,j}^{\pm}$	Ratio of $Q_{i,j}^{\pm}/P_{i,j}^{\pm}$ (FCT approach)	[M/T]
$\tilde{r}_{max}$	Maximum reaction rate related to biomass	[1/T]
S	Innercell slope of concentration (slope limiter approach)	$[M/L^2]$
$s_i$	Local coordinate in direction <i>i</i> (FEM)	[-]
$S_0$	Storativity	[-]
t	Time	[T]
T	Correction factor for antidiffusive mass flux (FCT approach)	[-]
$\theta$	Curvature (slope limiter approach)	[-]
Θ	Weighting of implicit terms in FD time integration scheme	[-]
au	Upwind coefficient (SUPG approach)	[-]
au	Transport rate (Iterative two-step coupling)	$[M/L^3/T]$
V	Volume	$[L^3]$
$\underline{v}_a$	Seepage velocity	[L/T]
$\underline{v}_f$	DARCY velocity	[L/T]
X	Biomass concentration related to pore volume	$[M/L^3]$
Y	Yield coefficient	[-]

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### Institut für Wasserbau **Universität Stuttgart**

Pfaffenwaldring 61 70569 Stuttgart (Vaihingen) Telefon (0711) 685 - 64717/64749/64752/64679 Telefax (0711) 685 - 67020 o. 64746 o. 64681 E-Mail: iws@iws.uni-stuttgart.de http://www.iws.uni-stuttgart.de

Direktoren Prof. Dr. rer. nat. Dr.-Ing. András Bárdossy Prof. Dr.-Ing. Silke Wieprecht

Vorstand (Stand 1.2.2008) Prof. Dr. rer. nat. Dr.-Ing. A. Bárdossy Prof. Dr.-Ing. R. Helmig Prof. Dr.-Ing. S. Wieprecht Prof. Dr.-Ing. habil. B. Westrich Jürgen Braun, PhD Dr.-Ing. H. Class Dr.-Ing. S. Hartmann Dr.-Ing. H.-P. Koschitzky PD Dr.-Ing. W. Marx Dr. rer. nat. J. Seidel

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Lehrstuhl für Hydrologie und Geohydrologie Leiter: Prof. Dr. rer. nat. Dr.-Ing. András Bárdossy Stellv.: Dr. rer. nat. Jochen Seidel

#### VEGAS, Versuchseinrichtung zur Grundwasser- und Altlastensanierung

Leitung: Jürgen Braun, PhD Dr.-Ing. Hans-Peter Koschitzky, AD

## Versuchsanstalt für Wasserbau

Leiter: apl. Prof. Dr.-Ing. habil. Bernhard Westrich

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- 1 Röhnisch, Arthur: Die Bemühungen um eine Wasserbauliche Versuchsanstalt an der Technischen Hochschule Stuttgart, und Fattah Abouleid, Abdel: Beitrag zur Berechnung einer in lockeren Sand gerammten, zweifach verankerten Spundwand, 1963
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