Reactive dispersive contaminant transport in coastal aquifers: Numerical simulation of a reactive Henry problem

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Abstract

The reactive mixing between seawater and terrestrial water in coastal aquifers influences the water quality of submarine groundwater discharge. While these waters come into contact at the seawater groundwater interface by density driven flow, their chemical components dilute and react through dispersion. A larger interface and wider mixing zone may provide favorable conditions for the natural attenuation of contaminant plumes. It has been claimed that the extent of this mixing is controlled by both, porous media properties and flow conditions. In this study, the interplay between dispersion and reactive processes in coastal aquifers is investigated by means of numerical experiments. Particularly, the impact of dispersion coefficients, the velocity field induced by density driven flow and chemical component reactivities on reactive transport in such aquifers is studied.

To do this, a hybrid finite-element finite-volume method and a reactive simulator are coupled, and model accuracy and applicability are assessed. A simple redox reaction is considered to describe the degradation of a contaminant which requires mixing of the contaminated groundwater and the seawater containing the terminal electron acceptor. The resulting degradation is observed for different scenarios considering different magnitudes of dispersion and chemical reactivity. Three reactive transport regimes are found: reaction controlled, reaction–dispersion controlled and dispersion controlled. Computational results suggest that the chemical components' reactivity as well as dispersion coefficients play a significant role on controlling reactive mixing zones and extent of contaminant removal in coastal aquifers. Further, our results confirm that the dilution index is a better alternative to the second central spatial moment of a plume to describe the mixing of reactive solutes in coastal aquifers.

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1. Introduction

Coastal aquifers are dynamic systems that are vulnerable to anthropogenic perturbations such as climate change, rising demand for freshwater, disruption of natural hydrological conditions, and groundwater contamination. Density driven flow and biogeochemical processes in such aquifers continue to receive attention as these aquifers are sensitive to salinisation of fresh groundwater by seawater intrusion, the disposal of waste and sewage, and the leaching of contaminants (Post, 2005; Werner et al., 2012). These processes are important controlling factors for the groundwater and coastal surface water quality (Moore, 1999). In particular, submarine groundwater discharge (SGD) provides a pathway for the transfer of nutrients from land to the coastal ocean (Burnett et al., 2003) and the reactions among the intruded seawater, fresh groundwater and porous media influence their concentration in SGD (Slomp and Van Cappellen, 2004). The processes at freshwater–seawater interface are thus important for determining subsurface pathways and fluxes of land-derived chemicals to the marine environment.

Many factors control the dynamics of the freshwater–saltwater interactions, including: density variations induced...
by seawater penetrating into the freshwater (e.g. Abd-Elhamid and Javadi, 2011; Reilly and Goodman, 1985); porous media heterogeneity (Diersch and Kolditz, 2002; Kerrou and Renard, 2010; Li et al., 2009; Mulligan et al., 2007); the width of the mixing zone (e.g. Abarca et al., 2007); seasonal fluctuations in influx of seawater and groundwater (Michael et al., 2005; Taniguchi et al., 2006); tidal effects (Attaie-Ashtiani et al., 2001; Boufadet al., 2011; Li et al., 2008; Lu et al., 2009; Robinson et al., 2007); dense contaminants leaking to the aquifer (e.g. Simmons, 2005); geothermal convection (Moore, 2010; Wilson, 2005); and the chemistry of the fluid and medium present in the system (e.g. Boluda-Botella et al., 2008; Rezaei et al., 2005; Santoro, 2010).

The mixing between freshwater and seawater in coastal aquifers is a key process controlling the chemistry of SGD. For mixing of non-reactive species in coastal aquifers, it has been claimed that the dispersive region along the freshwater–seawater interface is controlled mainly by the flow field and porous material properties such as dispersion coefficients (e.g. Kerrou and Renard, 2010). Pool et al. (2011) showed the significant contribution of transverse dispersion in creating mixing in the interface. Lu and Luo (2010) related the enhanced mixing to kinetic mass transfer between mobile and immobile phases. The detailed study of Abarca et al. (2007) revealed the controlling effects of longitudinal and transverse dispersion on the extent of the unreactive mixing zone. Held et al. (2005) also pointed out that dispersive mass transport from the seawater to the freshwater and the medium permeability govern the extension of the intruded seawater in the aquifer.

The knowledge on reactive mixing in contaminated aquifers, under steady state conditions, is also fairly advanced for density-independent problems. It has been suggested that the transverse dispersion controls the degradation of contaminant plumes (Cirpka and Valocchi, 2007; Shao et al., 2009), as well as the length of the plumes (Ham et al., 2004). Werth et al. (2006) showed that flow focusing in high permeability zones leads to a significant enhancement of transverse mixing and, hence, biodegradation capacity. Transverse dispersion at the fringe of contaminant plumes also limits the reactive mixing (Chiogna et al., 2011; Rolle et al., 2009) as do bioclogging processes (Thullner et al., 2004). The micromodel experiments on biomass growth conducted by Zhang et al. (2010) revealed that when the Damköhler number (Da, the ratio of the chemical reaction rate to the mass transfer rate) decreases, the reactive transverse mixing zone becomes wider. These results suggest that the reaction rate constant together with transverse mixing controls the total reaction rates in groundwater aquifers.

In contrast to density-independent groundwater, there is limited number of studies on reactive mixing for seawater intrusion problems. In coastal aquifers, flow is not only affected by dispersion but also by density variations. In other words, the dispersive density driven flow controls flow field as well as chemical mixing. For instance, a couple of field and numerical studies have shown that dispersion and density variation are important factors affecting nutrient fluxes into the sea (Andersen et al., 2005; Kroeger and Charette, 2008; Spiteri et al., 2008b). However, the mechanisms controlling reactive mixing in coastal aquifers remain poorly known. Their dynamic interplay should also be elucidated further as this will ultimately determine the qualitative significance of fluxes of land derived chemicals to the marine environment.

Over the last decade, several flow and transport codes have been coupled with multi-component reaction solvers to study reactive processes for seawater intrusion problems (Table 1). These models make use of various discretization methods as well as different coupling approaches for solving reactive transport problems (Table 1). The transport code based on structured grids does not lend themselves easily to model complex geometries and accurate velocity fields as they cannot easily represent inclined or curved geological features, such as fractures (Matthäi et al., 2009). Hence, the models based on unstructured mesh pose a more rigorous alternative to models based on structured grids. Flow and transport models utilizing a first-order scheme fail to preserve sharp concentration fronts, since the transport equation has a strongly hyperbolic character (e.g. Gudonov, 1959). This makes it desirable to extend the scheme to obtain higher-order accuracy, although higher order scheme may suffer from spurious oscillations (Matthäi et al., 2009). The previous numerical studies on coupled density driven flow and reactive transport problems are limited (Graf and Therrien, 2007; Post, 2005), and many of the most commonly used software focus either on transport phenomena or reactions (Wissmeier and Barry, 2011).

In this article, the main objective is to advance our qualitative understanding of reactive processes in coastal aquifers where seawater intrudes by density driven flow. For this purpose, two
flexible models are combined: a) the Complex System Modelling Platform (CSMP++) which can simulate both single- and multi-
phase flow in fractured and porous media (Matthai et al., 2009), and b) the Biogeochemical Reaction Network Simulator (BRNS)
capable of solving for kinetically and thermodynamically con-
strained biogeochemical reactions (Aguilera et al., 2005; Regnier et al., 2002). In this study, the combined model is employed to
study the combined effect of density driven flow, dispersion and
chemical reactions on transport and reactive processes in coastal
aquifers.

This paper is structured as follows. First, the governing
equations as well as the combined CSMP++ and BRNS model
are presented. Next the model is applied to the degradation of a
dissolved organic carbon (DOC) type contaminant along the
seawater interface of a coastal aquifer. Verification
of the developed coupled model by means of an analytical
solution and an accurate finite element approach are then
included. The combined effect of dispersion and reaction
dynamics on the degradation of DOC is quantified under
transient and steady state flow conditions for a wide range of
densities. Finally, the factors controlling the extent of the
reactive mixing region are identified.

2. Reactive transport modeling
2.1. Governing equations

Considering the effects of density and viscosity, Darcy’s
law reads,

\[ \mathbf{u} = -\frac{k}{\mu} (\nabla P - \rho \mathbf{g}) \],

(1)

where \( k \) is the intrinsic permeability tensor [L^2], \( \mu \) is the viscosity [ML^-1T^-1], \( \nabla P \) is the
pressure gradient, and \( \rho \) is the fluid density [ML^-3].
Parameter \( \mathbf{g} \) is the gravity vector [LT^-2]. Assuming a slightly
compressible fluid and a non-deformable porous medium,
conservation of mass is ensured by the continuity equation,

\[ \frac{\partial}{\partial t} \rho + \nabla \cdot (\rho \mathbf{u}) = 0 \],

(2)

where \( \rho \) is the density [ML^-3] and \( \mathbf{u} \) is the velocity [LT^-1]. \( \rho \) is the density
and \( \mathbf{u} \) is the unit tensor. \( \nabla \cdot \mathbf{u} \) is the divergence of the velocity vector.

Referring to the tortuosity of the porous media. The parameters \( \alpha_L \) and \( \alpha_T \) are the longitudinal and transversal dispersivities/ dispersion lengths [L], respectively. \( \mathbf{I} \) is the unit tensor, and \( |\mathbf{u}| \) is the magnitude of the velocity vector.

Eqs. (2) and (3) are coupled by the equations of state which
present the fluid density and viscosity as functions of mass
fraction, temperature and pressure (Diersch and Kolditz,
2002). Often the fluid density equation is expressed as a linear
function of the mass fraction (e.g. Abarca et al., 2007; Younes,
2003).

2.2. Numerical approach
2.2.1. BRNS

BRNS is capable of handling a comprehensive suite of
multi-component complexation (aqueous and surface) and
mineral precipitation and dissolution reactions, and is also able
to treat reaction networks characterized by partial redox dis-
equilibrium and multiple kinetic pathways (Centler et al., 2010;
Dale et al., 2009b; Thullner et al., 2005). BRNS has been applied
for reactive transport problems in porous media such as fate of
phosphorus in saturated aquifers (Spiteri et al., 2007), anaerobic
oxidation of methane in marine sediments (Dale et al., 2008),
organic matter mineralization pathways in marine sediments
(Thullner et al., 2009), influence of bioavailability limitations on
biodegradation at pore scale (Gharasoo et al., 2011), and de-
gradation of wellbore cements under CO₂ storage conditions
(Raoof et al., 2012). BRNS benefits from using a Maple interface
as a symbolic programming language. The Maple preprocessor
generates all the necessary Fortran files needed for solving the
reaction network. The method is explained in detail in Regnier
encapsulating the chemical solver of BRNS and the user defined
reaction network can be built and linked with other transport
codes (Centler et al., 2010).

Concentrations of reactive species, as well as stoichiometry,
rate parameters and equilibrium constants of the reactive
processes are used to define a specific reaction network. The
reaction term in Eq. (3) representing the sum of all reactions
affecting the concentration of a given species \( i \) can be written as:

\[ R_i = \sum_{m=1}^{N_{\text{reaction}}} q^m_i r_i, \]

(5)

where \( N_{\text{reaction}} \) is the number of reactions, \( q^m_i \) is the stoicho-
metric coefficient of component \( i \) in the reaction \( m \), and \( r_i \)
represents the rate of the reaction \( m \). If some of the reactions
considered are assumed to be at equilibrium, they can be
replaced with algebraic expressions based on mass action
expressions. By replacing one or more of the ordinary differen-
tial equations (ODEs) associated with reaction(s) with
algebraic relations based on a mass action expression in the
local equilibrium case, the set of ODEs is transformed into a set
of differential-algebraic equations (DAEs) (see Regnier et al.,
2002, for further details). Examples of applications include the
study by Spiteri et al. (2008c) for full equilibrium simulations
and the studies by Dale et al. (2009a) and Krumins et al. (2012)
for mixed kinetic-equilibrium cases. The form of rate expres-
sion, \( r_i \), is arbitrary, even nonlinear, and can be a function
of several concentrations within the system. The compiled library
contains the kinetic and equilibrium reactions. The generated Fortran files and the solver engine for solving a nonlinear set of equations ensued from kinetic of multi components are embedded in BRNS. The reactive solver uses a Newton–Raphson method to solve the set of kinetic and equilibrium reaction equations.

2.2.2. CSMP++

The computer code CSMP++ can simulate both single- and multi-phase 2D/3D flow and the resulting transport of dissolved species (Matthäi et al., 2004). It features an object-oriented application programmer interface (APL), designed for the simulation of complex geological processes and their interactions (Coumou et al., 2008; Geiger et al., 2010; Latham et al., 2012; Matthäi et al., 2007; Nick et al., 2011; Paluszny and Zimmerman, 2011). This geometrically flexible and stable transport algorithm can resolve complex geological structures and many orders of magnitude of permeability variations which are ubiquitous in geological formations (Geiger and Matthäi, 2012). CSMP++ relies on a non-oscillatory higher-order accurate finite-element node-centered finite-volume (FEVF) scheme for solving time-dependent advection–dispersion problems (Matthäi et al., 2009). An algebraic multigrid method for system of equations, SAMG, (Stüben, 1999) is employed as the solver for Eqs. (2) and (3).

Eqs. (2) and (3) are solved implicitly using an operator splitting method (Matthäi et al., 2009). First, we obtain the pressure field by solving Eq. (2) on a linear finite-element discretization. The pressure field can be solved in the weak splitting method (Matthäi et al., 2009). First, we obtain the

\[ \int_{\Omega} N^T \phi n d\Omega - \Delta t \int_{\Omega} \nabla N^T D \nabla n d\Omega \mathbf{c} = \left( \int_{\Omega} N^T \phi n d\Omega \right) \mathbf{c}^+ \]

(7)

where \( \mathbf{c}^1 \) and \( \mathbf{c}^{+} \) denote the distributed dependent variable, \( \mathbf{c} \), at time \( t \) and \( t + \Delta t \), respectively. For the advection term in Eq. (3), using piecewise constant FV interpolation functions, \( M_j \), for each finite-volume \( j \) and a first-order upwind scheme, integration over volume \( V \) gives,

\[ \phi \int_V M_j \mathbf{c}^{+ \Delta t} dV + \Delta t \int_V (\mathbf{n} u) \mathbf{c}^{+ \Delta t} dS = \phi \int_V M_j \mathbf{c}^1 dV + \Delta t \int_V \mathbf{c}^1 q dV. \]

(8)

where, \( \mathbf{n} \) represents the normal vector to the outward facing surface element. To make the transport scheme second-order accurate in space, we calculate estimates of the gradient of the transported variable for each control volume facet. Then, we apply the minmod slope limiter to suppress spurious oscillations that occur when the gradient of the transported variable is overestimated (Pain et al., 2003). This guarantees that the transport scheme becomes total variation diminishing (Matthäi et al., 2009).

CSMP++ hybrid element stencils allow for the assembly of finite volumes from arbitrary combinations of tetrahedral, prism, pyramidal and hexahedral elements which permit to simulate complex geological formations (Paluszny et al., 2007).

2.2.3. Numerical procedure

CSMP++ and BRNS are coupled to simulate reactive multi-component transport in heterogeneous porous media that are discretized with spatially variably refined unstructured grids to allow a realistic representation of the flow geometry. We compute transient flow, advection–dispersion and reaction in a sequential manner (e.g. Steefel and MacQuarrie, 1996).

Eqs. (2) and (3) are nonlinear as the fluid density affecting the velocity field is a function of the salt concentration. Therefore, a Picard iterative method is employed to linearize the equations (Putti and Paniconi, 1995). Within the iterative step, Eq. (2) is solved to obtain flow velocity field via Eq. (1). Next, the multi-component advection–diffusion Eq. (3), describing solute transport is solved employing a hybrid FEFVM for the components that may affect the flow field. This is because the flow field needs to be recalculated if the porous media properties, such as porosity and permeability, and fluid properties, such as fluid density and viscosity, change as a consequence of transport or reactions (e.g. Nick et al., 2009).

After the iterative procedure has converged, the Eq. (3) is solved for the components which do not affect the flow equation. Applying sequential non-iterative operator splitting, in each time step first the transport solution is obtained and then the reaction part is solved using the reactive solver of BRNS. In order to eliminate possible operator splitting errors the Courant number condition, which is defined as \( u \Delta t / \Delta x < 1 \), is imposed during the simulations (Xu et al., 1999). Since the concentrations are piece-wise constant within each finite-volume, the concentrations of the components at every node are assembled for BRNS to solve for one reaction time step. BRNS updates the
concentration of reactive components for the next transport time step (Fig. 1). In principal, similar to Mao et al. (2006), the fluid density and viscosity as a function of species concentration can be evaluated. However, in this work for the sake of simplicity we utilize a linear function, as equation of state for fluid properties, only to consider the effect of salt concentration on fluid density as, \( \rho = \rho_0 + \omega (\rho_{\text{max}} - \rho_0) \), where \( \omega \) denotes salt mass fraction, and \( \rho_{\text{max}} \) and \( \rho_0 \) are the maximum (\( \omega = 1 \)) and initial fluid densities (\( \omega = 0 \)), respectively.

### 2.3. Numerical experiments

Four 2D models of the reactive Henry problem introduced here (Table 2) are used to examine mechanisms controlling the fate of nutrient transport in coastal aquifers. These models are utilized for the verification of the simulation method as well as for studying the reactive transport at the seawater freshwater mixing zone in coastal aquifers. Note that the Henry problem is yet a simplified model, however, in order to present a more suitable description of the saltwater intrusion problem in coastal aquifers both velocity dependent dispersion and reaction are included.

#### 2.3.1. Verification, conservative steady state problem

A vertical cross section through a homogeneous confined aquifer (Model 1), 2 m × 1 m, is meshed with rectangular elements (element size of 5 cm, Fig. 2). Hydrostatic field pressure affected by density gradients leads to seawater intrusion into the model domain through the right boundary (Dirichlet boundary condition), while a constant flux of groundwater (\( 3.3 \times 10^{-5} \text{m}^2\text{s}^{-1} \)) is assigned along the left boundary. Like Simpson and Clement (2004), flow and porous medium properties are the same as for the modified Henry problem. Permeability, porosity, and molecular diffusion are \( 1 \times 10^{-9} \text{m}^2 \), 0.35 and \( 1.886 \times 10^{-5} \text{m}^2\text{s}^{-1} \), respectively. A maximum density ratio of 1.025 between seawater and freshwater.
redox reaction: analogy with the case three of Slomp and Van Cappellen (2004) conservative tracer, both of 1 mM. This scenario is chosen by Anoxic groundwater contains dissolved organic carbon, and a common end-member case in such aquifers (Charette et al., 2005; Spiteri et al., 2006; Uchiyama et al., 2000).

2.3.2. Verification, reactive transient problem

To verify the combined CSMP-BRNS model (Model 2), a redox reaction:

\[ \text{DOC} + O_2 \rightarrow \text{CO}_2 + H_2O. \]

is solved by CSMP-BRNS employing the FEFVM as well as COMSOL Multiphysics (COMSOL, 2005; Hayek et al., 2012) using a FEM. In the simulations seawater contains O$_2$ of 0.2 mM. Anoxic groundwater contains dissolved organic carbon, and a conservative tracer, both of 1 mM. This scenario is chosen by analogy with the case three of Slomp and Van Cappellen (2004) where anoxic groundwater meets oxic seawater, representing a common end-member case in such aquifers (Charette et al., 2005; Spiteri et al., 2006; Uchiyama et al., 2000).

The rate law is defined as (Hunter et al., 1998):

\[
 r = \begin{cases} 
 K_{\text{DOC}} \text{[DOC]} & \text{if } [O_2] > K_{\text{M}O_2}, \\
 K_{\text{DOC}} \text{[DOC]} & \text{else}
\end{cases}
\]

where $K_{\text{DOC}}$ is the rate constant for decomposition of DOC, and $K_{\text{M}O_2}$ is the limiting concentration of O$_2$. $K_{\text{M}O_2} = 3.0 \times 10^{-2}$ mM, and $K_{\text{DOC}} 1.0 \times 10^{-3}$ s$^{-1}$ are used in this example.

2.3.3. Transient reactive transport — dispersion sensitivity

Anthony (2004) and Abarca et al. (2007) have addressed the effect of longitudinal and transversal dispersivities on non-reactive seawater intrusion. Here, in order to evaluate this effect for reactive transport, different combinations of dispersion coefficients are used to investigate the controlling behavior of these coefficients on reactive mixing between seawater and fresh groundwater. Note that some of these values used in this study are selected for demonstration purposes and sensitivity analysis.

As in the previous model, aerobic degradation Eq. (9) is simulated; but now for a transient injection of DOC (Model 3). At steady state conditions for the flow, DOC is injected for 1 h through the left boundary at a concentration of 1 mM. These simulations are conducted for porous media with different combinations of high (h) and low (l) dispersivity values: L$_h$T$_h$ (a$_h$ = 1 mm and a$_l$ = 1 mm), L$_h$T$_l$ (a$_h$ = 10 cm and a$_l$ = 1 mm), L$_l$T$_h$ (a$_l$ = 1 mm and a$_l$ = 10 cm), and L$_l$T$_l$ (a$_l$ = 10 cm and a$_h$ = 10 cm). Here, the abbreviations L and T stand for longitudinal and transversal dispersivities, respectively.

Note that a constant flux of fresh groundwater $6.0 \times 10^{-5}$ m$^2$s$^{-1}$ and the molecular diffusion value of $1 \times 10^{-9}$ (m$^2$s$^{-1}$) are used for all these following simulations. The model mesh is also refined further and an element size of 2.5 cm is used.

2.3.4. Steady state reactive transport — reaction rate sensitivity

The effect of dispersivity and aerobic degradation rate, $K_{\text{DOC}}$, is analyzed by comparing the results obtained for simulations that combine longitudinal dispersivities of 1 mm or 10 cm with transversal dispersivities of 1 mm, 1 cm or 10 cm for different $K_{\text{DOC}}$ values ranging from $1.0 \times 10^{-3}$ to $1.0 \times 10^{-9}$ s$^{-1}$. Here DOC is injected continuously and simulations are carried out until steady state is achieved for all components (Model 4).

2.4. Analysis strategy

Following the study of Abarca et al. (2007) three different characteristic parameters are calculated: 1) Dimensionless toe penetration of saltwater, $L_0 = L_{\text{toe}}/d$, which is the penetration of the seawater intrusion wedge, $L_{\text{toe}}$, measured as the distance between the seaward boundary and the point where the 50% mixing isoline intersects the aquifer bottom, normalized by the model width, d. 2) Normalized averaged width of the mixing

Table 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Model 1</th>
<th>Model 2</th>
<th>Model 3</th>
<th>Model 4</th>
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<td>Diffusion</td>
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<td>cm</td>
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<tr>
<td>$K_{\text{DOC}}$</td>
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<td>-</td>
<td>$10^{-5}$</td>
<td>$10^{-6}$</td>
<td>$10^{-9}$</td>
</tr>
</tbody>
</table>


and a freshwater density of 1000 kg m$^{-3}$ is used for all examples in this work. Note that the seaward boundary condition for concentrations switches between Dirichlet and Neumann conditions depending on the flow direction at the boundary (Volker and Rushton, 1982).

![Fig. 2. Domain and the variables used for analysis of the Henry saltwater intrusion problem. Shown mesh of rectangular elements corresponds to the spatial discretization used in Model 1.](image-url)
zone $W_0$ as the average of the vertical distance $W$ between iso-concentration lines of 25% and 75% concentration between 0.2 LD and 0.8 LD divided by d. 3) Saltwater/freshwater discharge ratio, $R_D$ (Fig. 2).

2.4.1. Dilution index

Kitanidis (1994) introduced the dilution factor to measure the true mixing which is defined as:

$$E = \exp\left(-\int_\Omega \ln P \, dx\right).$$

(10)

where $P = c(x,y)/\int_\Omega c(x,y) \, dx$ is the normalized concentration field by the integrated mass.

The index $E$ is a measure for both, the area over which the mass of a tracer is distributed, and its uniformity. This index is larger for enhanced uniform dilution. It is referred to as "true mixing" as the macro dispersion model employing macro dispersivities based on second central spatial moments of a plume result in an overprediction of mixing-controlled reaction rates (Cirpka et al., 1999).

3. Results and discussion

3.1. Verification

First, seawater intrusion into a homogeneous domain is verified against semi-analytical solution of the modified Henry problem (e.g. Kolditz et al., 1998). This, further, is compared with the solution obtained using COMSOL Multiphysics to verify CSMP-BRNS against a standard finite element approach.

3.1.1. Steady state problem

The modified Henry problem (Simmons, 2005) is solved employing both CSMP-BRNS and COMSOL (Holzbecher, 2005). Seawater intrudes from the seaward boundary until a steady state between the denser intruded fluid and the lighter recharging fluid is reached. The iso-concentration contours are shown in Fig. 3. Both CSMP-BRNS and COMSOL model results agree well with the semi-analytical solution of the modified Henry problem presented by Simmons (2005). This verification step shows that the CSMP-BRNS can solve accurately 2D stable variable-density problems.

3.1.2. Nonconservative transient problem

This test case compares the transient distribution of non conservative species achieved with CSMP-BRNS against a well tested numerical approach, COMSOL. The objective is to compare the CSMP-BRNS using sequential non-iterative approach (e.g. Walter et al., 1994) against COMSOL using fully coupled algorithm, in which chemical equations are directly substituted into the transport equations so that they are solved simultaneously, for both transport and reaction processes (e.g. Steefel and Lasaga, 1994). Here, the transient simulation is conducted for density flow transport and reaction. Aerobic degradation results from the injection of DOC on the landward boundary, which is injected for 1 h at a concentration of 1 mM, and $O_2$ on the seaward boundary. As a result of the reaction dissolved inorganic carbon (DIC) is produced (Eq. (9)). Fig. 4 reveals that the DOC, $O_2$ and DIC concentration fields after 2 h for both models are in good agreement. This is confirmed by $L^2$ norms, $\|c_{FEFVM} - c_{FEM}\| = \sqrt{\sum_{i=1}^{i=N} (c_{FEFVM} - c_{FEM})^2}$, of 0.0267, 0.0431, and 0.0079 for DOC, $O_2$ and CO$_2$, respectively. While the fully coupled approach is restricted to simple problems due to large memory requirements (Bell and Binning, 2004), CSMP-BRNS provides the required flexibility to model multi-component reactive flow problems in geological media. Geiger et al. (2009) is an example of utilizing CSMP for multi-component multiphase flow problems in fractured porous media. In addition, CSMP-BRNS has been implemented in an object-oriented simulator, whose modular design allows for further enhancements and extensions (Matthäi et al., 2007).

3.2. Dispersivity effects on density driven flow, transport and reaction

Here, we identify the role of longitudinal and transversal dispersivity on transport and, then, reaction for a density

![Fig. 3. Steady state iso-concentration contours calculated with FEFVM (CSMP-BRNS), FEM (COMSOL) and the semi-analytical solution are shown. The two dimensional model is discretized by rectangular elements (Model 1). Note that, in order to be consistent with the semi-analytical solution of the Henry problem, a Dirichlet boundary condition is applied for the salt concentration at the seaward boundary.](image-url)
driven flow setup. Several transient simulations are conducted for porous media with different combinations of high and low values for the dispersivities. Results show that the dimensionless toe penetration of saltwater \( (L_D) \) decreases with increasing dispersion coefficients (Table 3). As expected, the normalized averaged width of the mixing zone \( (W_D) \) and the saltwater/freshwater flux ratios \( (R_D) \) become larger for the cases with higher dispersion. The results also show that the \( L_D \) reduction due to an increase of the transversal dispersivity is more significant when the longitudinal dispersivity value is high. While the \( L_D \) and \( R_D \) are sensitive to both dispersivity values, the \( W_D \) is mainly controlled by the transversal dispersivity only. The small effect of longitudinal dispersivity is limited to high salinity zones. This is in agreement with the results of Abarca et al. (2007). Velocity field and salt concentration distributions are strongly affecting each other. Considering the dispersive flux term in Eq. (3) together with the Scheidegger formulation for calculating the dispersion Eq. (4), reveals that transverse dispersion is dominant where the velocity field is perpendicular to the salt concentration gradient. In contrast, longitudinal dispersion is affecting the flow and transport where the salt concentration gradient is parallel to the velocity vectors. Thus, as shown in Fig. 5, the saltwater intrusion toe area, and the zone below the interface at the vicinity of the counter line of 90% concentration are two regions of the domain where longitudinal dispersion should be dominant. However, the fact that the velocity vectors are about two orders of magnitude smaller here than the velocity vectors in the freshwater zone, explains why the influence of longitudinal dispersivity on concentration distribution is limited.

Fig. 6 shows the effect of dispersion coefficients on the DOC degradation rate (Model 3). The transient results clearly show that larger mixing coefficients enhance the efficiency of the degradation process. In particular, increasing transversal dispersivity widens the reaction zone where the velocity vectors are parallel to the interface between saltwater and freshwater, while increasing longitudinal dispersivity causes a broader reaction zone at the toe of the penetrated seawater where the velocity vectors are more perpendicular to the interface (Fig. 5). This is further substantiated in Fig. 7 which shows breakthrough curves of DOC and tracer concentrations for the four dispersivity scenarios. These breakthrough curves are obtained at the freshwater outflow along the right boundary of the model. Increasing the longitudinal dispersivity values causes anomalous transport, longer tailing, for all components. On the other hand, increasing dispersivities lowers the peak in the breakthrough curves and widens the mixing zone, resulting in enhanced degradation of DOC. In Fig. 5 it can also be seen that the velocity vectors, which are normal to the concentration gradient, are larger in the freshwater zone near the interface. This explains why the reactive mixing zone is more developed into the freshwater zone, leading to an asymmetric concentration distribution in the mixing zone (Fig. 6).

3.3. \( K_{DOC} \) and dispersion effects on degradation rate

In Fig. 8, the scaled aerobic degradation rate \( (R/K_{DOC}) \) profiles at \( x = 0.5 \ L_D \) are illustrated for combinations of different dispersion coefficients and reaction rate parameters. Comparing Fig. 8a and b reveals that increasing longitudinal dispersivity expands slightly the width of the mixing zone towards the seawater zone. This effect is more pronounced when \( K_{DOC} \) is low and, thus, longitudinal dispersivity is less influential on reactive mixing for fast reactions. An increase in transversal dispersivity widens the reactive mixing zone significantly and this spreading is larger when \( K_{DOC} \) is low. While increasing longitudinal dispersivity has negligible impact on the maximum value of the scaled aerobic degradation rate, increasing transversal

---

**Table 3**

<table>
<thead>
<tr>
<th>Scenarios</th>
<th>( L_D )</th>
<th>( W_D )</th>
<th>( R_D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L_1T_1 )</td>
<td>1.65</td>
<td>0.05</td>
<td>0.06</td>
</tr>
<tr>
<td>( L_hT_1 )</td>
<td>1.58</td>
<td>0.05</td>
<td>0.09</td>
</tr>
<tr>
<td>( L_1T_h )</td>
<td>1.04</td>
<td>0.22</td>
<td>0.30</td>
</tr>
<tr>
<td>( L_hT_h )</td>
<td>0.90</td>
<td>0.29</td>
<td>0.33</td>
</tr>
</tbody>
</table>

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**Fig. 4.** a) DOC, b) \( \text{O}_2 \), and c) DIC iso-concentration contours calculated with the FEFV and FE methods after 7200 s (Model 2).
dispersivity enhances it. This effect is most substantial for fast reactions.

The volume-averaged degradation rate, \( <R> \), increases with increasing dispersivities because enhanced mixing forces the decomposition process. As expected, transversal dispersivity has more influence on the averaged rate than longitudinal dispersivity (Fig. 9). To study the effect of K\(_{\text{DOC}}\) on averaged reaction rate, the Damköhler number, \( \text{Da} = \frac{K_{\text{DOC}}L_{\text{geo}}}{F_{\text{sw}}} \) is used, where \( F_{\text{sw}} \) is the seawater-flux through the seaward boundary. For the lowest value of the Da number, the dispersivity values control the reactive mixing, while the reactive rate, \( K_{\text{DOC}} \), is the controlling parameter for the higher value of the Da number. The regime shift occurs at \( \text{Da} > 4 \) and \( \text{Da} < 0.2 \) for the reaction controlled and dispersion controlled regimes, respectively. Intermediate Da numbers correspond to a reactive mixing controlled by both \( K_{\text{DOC}} \) and the dispersion. The linear proportionality of \( <R> \) to \( K_{\text{DOC}} \) for slow reactions, confirms that the dispersive reactive mixing is not limited by kinetics. This is different for fast reactions as the dispersive reactive mixing is limited by kinetics.

Fig. 8 provides further insight into the reactive mixing dynamics. For \( K_{\text{DOC}} \) values within the range of \( 1.0 \times 10^{-3} - 1.0 \times 10^{-5} \text{ s}^{-1} \), a decrease in the rate constant increases the width of the reactive mixing zone. This explains why the scaled averaged rate decreases when \( K_{\text{DOC}} \) increases. However, lowering further the \( K_{\text{DOC}} \) has no effect on the scaled averaged rate.

![Velocity distribution at the seawater/freshwater interface](image1)

**Fig. 5.** Velocity distribution at the seawater/freshwater interface is shown for the subdomain \((0.5 < x < 1.0 \text{ m}, 0 < y < 0.5 \text{ m})\) of Model 3. Contour lines of 10% and 90% concentration are depicted in red \((\alpha_L = 1 \text{ mm} \text{ and } \alpha_T = 1 \text{ mm})\).

![Degradation rates](image2)

**Fig. 6.** Aerobic degradation rates for the four scenarios with different dispersion coefficients are illustrated after 2.5 h: a) \( L_{\text{h}} T_{\text{h}} \), b) \( L_{\text{h}} T_{\text{t}} \), c) \( L_{\text{t}} T_{\text{h}} \) and d) \( L_{\text{t}} T_{\text{t}} \) (Model 3).
because the mixing zone width stays unchanged (Fig 8), and the scaled averaged rate is then only sensitive to the dispersivity values. Fig. 8a also shows an asymmetric reaction zone which moves towards the groundwater zone as $K_{DOC}$ values decrease. Thus, while the asymmetric shape of the reaction zone is governed by inhomogeneous dispersion induced by the flow field along the freshwater–seawater interface, the reactivity controls the location of the reaction zone.

The behavior of the reactive Henry problem is further illustrated in Fig. 10. As already shown in Fig. 8, faster reactions confine the reactive mixing zone to a narrower zone (Fig. 10a). The reaction zone also moves towards the fresh groundwater region when $K_{DOC}$ decreases, as the dispersion in this region is larger than the dispersion in the seawater zone, showing that its position is sensitive to the rate constant (Fig. 10b). An increase in longitudinal dispersivity advances the mixing zone into the seawater intruded area and leads to a receding toe penetration (Fig. 10c). The transversal dispersivity has a more pronounced effect on the mixing zone (see also, Abarca et al., 2007; Held et al., 2005; Werth et al., 2006). Although it also limits the seawater penetration, the mixing zone advances into the fresh groundwater zone (Fig. 10d). In general, a higher dispersion widens the mixing zone overlapping between reactants, but limits penetration of seawater into the aquifer.

3.3.1. True mixing

The dilution index, $E$, Eq. (10), as a measure of the degree of true solute mixing, is calculated based on the simulations for different dispersivity and $K_{DOC}$ values. The dilution factor calculated from the tracer results for each combinations of dispersivity coefficients is used to normalize the $E$ values for the $O_2$ concentration in Fig. 11a. This normalized value describes how complete is the dilution compared to the dilution of the tracer concentration. The mixing decreases by increasing the reaction rate constant. It is however less affected for constant reaction rates lower than $10^{-6}$ s$^{-1}$, illustrating a well mixed regime where the effect of chemical reactivity on true mixing is less pronounced. The significant reduction of the dilution index for the incompletely mixed regime and its sensitivity to both chemical reactivity and dispersivity values imply that both the chemical and porous media properties are of utmost importance in controlling the true mixing.

Similar to the dilution index, the second central spatial moment values are calculated. No meaningful relationship is obtained between the second moment values and the total degradation rates (not shown). A strong relation between the normalized dilution index and total degradation rate scaled by $K_{DOC}$ values is found. This can be seen in Fig. 11b where the dilution indices are plotted against the scaled total degradation rates. The scaled total rate is linearly proportional to the scaled dilution index. Altering transversal dispersivity affects the degree of this proportionality. Kitanidis (1994) suggested that the second central spatial moment may fail to explain the mixing of reactive solutes in porous media. Our result that the total degradation rate is proportional to the dilution index but not to the second spatial moment, also confirms this. However, a broader study is needed to explore the relationship between the dilution index and reactive flow parameters.

3.3.2. Future work

The simulations are limited to the study of a single kinetic process coupled to a density-driven flow and transport problem. Although reactive processes are undoubtedly more complex in natural settings, this description is nevertheless sufficient and realistic to elucidate the behavior of reactive mixing in coastal aquifers (Dai et al., 2012; Spiteri et al., 2008a). In the future, additional processes such as precipitation, dissolution, and formation of biofilms could be included as they remain to be studied in the context of reactive seawater intrusion problems. In addition, the effects of larger scale heterogeneity such as, fractures and impermeable lenses, could be addressed with CSMP-BRNS as this model is specifically geared to include discontinuities at the material interfaces (Nick and Matthäi, 2011a).

In this study, the homogeneous Henry problem model is used, to minimize confounding variables. Future research should expand to field scale models. Kerrou and Renard (2010) also pointed out that the results of dispersive seawater intrusion in two-dimension (2D) can be extrapolated to three-dimensions (3D) provided that the permeability field is rescaled and dispersivity values are modified accordingly. The relevance of our 2D results for the reactive mixing case will nevertheless require further assessment in the context of 3D applications.
Fig. 8. Steady state scaled aerobic degradation rate profiles at x = 0.5 Lc for different dispersion coefficient combinations (Model 4). Normalized concentration profiles are also plotted. a) L1T1, b) LhT1, c) L1Th and d) LhTh.
We present the accuracy and potential of CSMP-BRNS for a simplified example. The combined model presented here, however, is applicable to a wide range of flow and multi-component transport problems in geological media since it maintains the full flexibility of the original models. Yet, performing potential of CSMP-BRNS for more complex applications in coastal aquifers needs further demonstration.

4. Conclusions

The CSMP-BRNS model developed in this study is a simulation tool applicable to multi-component reaction-transport density-dependent flow in porous media. Using this model, we investigate the interaction between density driven flow, dispersion and reactive transport.

Similar to reactive-transport in density-independent groundwater systems:

- The Damköhler number as well as dispersivity parameters are important parameters governing the biogeochemical dynamics in the reaction zone and release of land-derived chemicals into coastal waters. Our findings suggest three dispersive mixing reactive regimes: 1) Dispersion controlled regime; 2) Reaction–dispersion controlled regime; and 3) Reaction controlled regime.
- The dilution index appears to be a good predictor for reactive mixing in the seawater intrusion problem.

In contrast, in seawater intrusion systems:

- An increase in longitudinal and transverse dispersion widens the mixing zone but shortens the length of the interface between seawater and freshwater, due to rather complex density driven flow. The effect of transverse dispersion is more significant.
- The reactivity of the chemical compounds also plays a significant role on the position and shape of the reactive mixing zone and, ultimately, on the averaged rates and export fluxes in reaction controlled regime. Decreasing chemical component reactivity considerably moves the position of the reaction zone towards freshwater.

Fig. 9. Averaged aerobic degradation rates scaled by KDOC versus Da number at steady state (Model 4) for different scenarios with different combinations of high (h), medium (m), and low (I) dispersivity values: L1T1 (αL = 1 mm and αT = 1 mm), LhT1 (αL = 10 cm and αT = 1 mm), L1Th (αL = 1 mm and αT = 10 cm), LhTh (αL = 10 cm and αT = 10 cm) and LhTm (αL = 10 cm and αT = 1 cm).

Hence, accounting explicitly for combined effect of dispersion and reaction in upscaled modeling of SGD using models with sharp interfaces or box models is essential.

Acknowledgments

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Fig. 11. Normalized dilution index calculated for different dispersivity combinations versus a) $K_{DOC}$ values, and b) integrated scaled aerobic degradation rate (Model 4).

References


