Transport of volatile compounds in porous media in the presence of a trapped gas phase

Olaf A. Cirpka a,b.*, Peter K. Kitanidis a

a Department of Civil and Environmental Engineering, Stanford University, Stanford, CA 94305-4020, USA
b Institut für Wasserbau, Universität Stuttgart, 70550 Stuttgart, Germany

Received 17 February 2000; received in revised form 8 November 2000; accepted 5 December 2000

Abstract

The presence of an immobile gaseous phase in an otherwise-saturated porous medium affects the transport of volatile compounds. The linear theory of partitioning tracers suggests that a volatile tracer introduced into such a system should be retarded with a constant retardation factor. Using high concentrations, however, the saturation of the gaseous phase will change as an effect of the tracer test itself. Competitive gas transfer among all volatile compounds and the change of saturation may lead to tracer concentrations that are temporarily higher than those injected. We analyze the system in the framework of the coherence theory by Helfferich [Soc. Pet. Eng. J. 21 (1) (1981) 51]. The governing equations are formulated as functions of total concentration, i.e., the mass of solutes in all phases per pore volume. Neglecting dispersion and mass-transfer kinetics, we derive the characteristic form of the resulting system of hyperbolic equations. In a system with \( N \) volatile compounds, a variation of the concentrations splits up into \( N \) waves, each traveling with its own characteristic velocity. If the presence of a gaseous phase is sustained, one wave will be a standing one. We perform numerical model calculations for tracers with various Henry's law coefficients and show that the results agree with the semi-analytical solution obtained by coherence theory. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Solute transport; Porous media; Gas transfer; Partitioning tracer; Coherence theory; Shock waves

* Corresponding author. Present address: Institut für Wasserbau, Universität Stuttgart, 70550 Stuttgart, Germany. Tel.: +49-711-685-8218; fax: +49-711-685-7020.
E-mail address: olaf.cirpka@iws.uni-stuttgart.de (O.A. Cirpka).

0169-7722/01/$ - see front matter ©2001 Elsevier Science B.V. All rights reserved.
PII: S0169-7722(00)00196-0
1. Introduction

Consider a partially saturated porous medium, i.e., the pore-space is occupied by water and gas. The volume occupied by a specific phase divided by the pore volume is referred to as its saturation. If the gas saturation is smaller than the residual one, the gas is trapped, i.e., it cannot flow. A trapped gas phase may have remained from a previously mobile one after imbibition of an unsaturated porous medium. It may also be the result of in-situ gas production from biochemical reactions or decompression of water that was saturated with a volatile compound. The presence of the immobile gas leads to significant retardation of solutes that partition into the gaseous phase (Fry et al., 1995, 1996; Donaldson et al., 1997, 1998) and may impair the performance of sand filters or fixed-bed reactors (Bello-Mendoza and Castillo-Rivera, 1998).

For the quantification of entrapped gas, Fry et al. (1995, 1996) and Donaldson et al. (1997, 1998) applied the technique of partitioning tracer tests, which is now well accepted in the quantification of non-aqueous phase liquid (NAPL) saturations (see, e.g., Jin et al., 1995). Fry et al. (1995) injected a pulse of dissolved oxygen at the solubility limit of pure oxygen gas into a partially saturated column. Fry et al. (1996) applied the method to a two-dimensional sandbox model. Donaldson et al. (1998) modified the experimental approach by using dissolved hydrogen at the solubility limit as the tracer. The analysis of Fry et al. (1995, 1996) was based on the following assumptions:

1. The aqueous phase is mobile, whereas the gas phase is immobile.
2. Mass-transfer between the aqueous and gaseous phases is instantaneous (local equilibrium assumption).
3. The partitioning between the phases is described by Henry’s law.
4. The volume occupied by each phase is not altered by the experiment.

Under these assumptions, transport of a gas-partitioning compound \( i \) can be described by:

\[
R_i \frac{\partial c_i}{\partial t} + \nabla \cdot (\nu c_i - D \nabla c_i) = 0
\]  

in which \( R_i [-] \) and \( c_i [\text{mol/m}^3] \) are the retardation factor and aqueous-phase concentration of compound \( i \), respectively; \( t [\text{s}] \) is time, \( \nu [\text{m/s}] \) is the seepage velocity vector, and \( D [\text{m}^2/\text{s}] \) is the dispersion tensor. Experimentally, the retardation factor of a partitioning compound \( i \) can be evaluated by comparing its mean arrival time \( t_i [\text{s}] \) to that of a non-partitioning tracer:

\[
R_i = \frac{t_i}{t_c}
\]  

in which \( t_c [\text{s}] \) is the mean arrival time of a conservative tracer transported exclusively in the aqueous phase. If the retardation factor varies in space, Eq. (2) describes its value
averaged along the path from the point of injection to that of observation. Neglecting surface sorption, the retardation factor \( R_i \) of compound \( i \) is related to the saturation \( S_k \) [-] of the gaseous phase by (Fry et al., 1995):

\[
R_i = 1 + \frac{\text{H}_i \, S_k}{\mathcal{R} \, T \, (1 - S_k)}
\]  

(3)

in which \( H_i \) [Pa m³/mol] is the compound-specific Henry’s law coefficient, \( \mathcal{R} \) is the ideal-gas constant of 8.314 Pa m³/(mol K) and \( T \) [K] is the absolute temperature.

In the experiments of Fry et al. (1995, 1996), the measured retardation factor of oxygen was higher than that anticipated from Eq. (3) when the gas saturation was 5% or higher. The authors identified kinetic gas transfer as a factor contributing to a delayed breakthrough, but suspected also that the gas saturation might have changed during the course of the experiments. Donaldson et al. (1997, 1998) presented a kinetic gas-transfer model and applied it to their experimental data. The model results fitted the shape of the oxygen breakthrough curves well. However, the authors also reported a change of gas saturation when helium was the entrapped gas (Donaldson et al., 1997) or hydrogen the gas tracer (Donaldson et al., 1998). A change of gas saturation was not included in their model.

In this study, we analyze the transport of volatile compounds in porous media in the presence of trapped gas based on the theory of multi-component mixtures in multi-phase systems by Helfferich (1981). Neglecting dispersive transport and mass-transfer kinetics, the coupled transport of all compounds partitioning into all phases is described by a system of hyperbolic equations. Any variation of the composition will be split into its characteristic components propagated with the corresponding characteristic velocities. Variations of all compounds propagated with the same velocity are called coherent waves, a term originally developed in the context of multi-component chromatography (see, e.g., the review by Helfferich and Whitley, 1996). In chromatography, the transport equations of the dissolved compounds are coupled because only a limited number of sites are available in the stationary phase; as a consequence, the sorption behavior of a specific compound is affected by the presence of competing sorbates. Since the transport equations of all sorbing compounds are coupled, the coherent waves consist of variations of compound mixtures rather than pure compounds, and the characteristic velocities differ from the effective velocities of single compounds.

In mass-transfer between water and trapped gas, the number of sites in the immobile gaseous phase is determined by the gas saturation. The gas saturation itself depends on the total amount of volatile compounds and tends to increase with the mass per pore volume of a specific volatile compound, the total concentrations of the other compounds remaining the same. That is, if we alter the total concentration of one compound, the gas saturation \( S_{ik} \) changes, and therefore also the retardation factor \( R_i \) of all compounds \( i \) undergoing partitioning. The linear theory of partitioning tracers, as applied in the studies of Fry et al. (1995, 1996) and Donaldson et al. (1997, 1998), is valid only at the limit of no change in the gas saturation. We will show that this assumption does not hold if volatile tracers are injected in concentrations approaching their solubility limits.
The objective of this study is to analyze transport of volatile compounds in the presence of a trapped gas phase for a significant and abrupt change in the concentration of a single or several volatile compounds. In Section 2, we describe an experiment of sulfur-hexafluoride injection into a partially saturated soil column (Hofmann, 1996; Josef, 2000). In Section 3, we discuss the governing equations. We solve these equations in Section 4 by a numerical method, and we analyze the developing waves of concentration changes by a semi-analytical approach based on coherence theory in Section 5. We demonstrate how the developing waves differ with the Henry's law coefficient of the introduced compounds in Section 6.

2. Experiment of SF₆-injection into a sand column

We describe an experiment performed at VEGAS, the research facility for subsurface remediation at the University of Stuttgart, Germany (Hofmann, 1996; Josef, 2000). Sandboxes, utilized as physical aquifer models, are filled with dry or slightly wet sand and water is injected until saturated conditions are reached. During this process, gas is entrapped in the porous medium affecting both water flow and the transport of volatile organic compounds. The investigators wanted to determine the saturation of the trapped gas phase by performing a tracer test with sulfur hexafluoride (SF₆) as partitioning tracer and fluorescein as non-partitioning. Volatile, poorly soluble compounds, such as SF₆, appear to qualify as partitioning tracers for the quantification of immobile gas, since

**Fig. 1.** Measured SF₆ concentrations as function of dimensionless time (modified after Josef (2000)).
these compounds are linearly distributed between water and gas according to Henry’s law (Stumm and Morgan, 1996).

The experiment was performed in a vertical column, 0.92 m long and 0.19 m in diameter, filled with medium-grain sand. Pure SF₆ gas was bubbled into degasified water that was assumed at equilibrium with air at \( \approx 25 \) kPa (25% of atmospheric pressure). The specific discharge was \( 3.66 \cdot 10^{-5} \) m/s and the porosity 0.36. Fig. 1 shows the SF₆ inflow and outflow concentrations, normalized by the average inflow concentration, as function of dimensionless time \( \tau \), which is the time after the start of injection divided by the time of 50% fluorescein breakthrough. The tracer broke through after about 25 pore volumes. Obviously, SF₆ did not behave in accordance with the linear theory of partitioning tracers. For a while, the concentration at the outflow was higher than at the inflow, and came down to the inflow value after about 45 pore volumes. The temporary enrichment of SF₆, i.e., the elevation of the concentration above the inflow value, is inconsistent with the model of simple retardation of SF₆. As we will discuss in Section 5, transport and partitioning of all volatile compounds are coupled, so that the behavior of a single compound, the tracer, cannot be considered independently of the others. In the experiment of Hofmann (1996), the aqueous-phase concentrations of the dominant air components, nitrogen and oxygen, were significantly different in the injected water than in the column prior to the injection. Hence, the change of concentrations of these compounds should be included in the analysis. Most importantly, the saturation of the gaseous phase may change as an effect of the tracer test itself.

3. Governing equations

Assume partitioning of the volatile compounds between the aqueous and gaseous phase according to Henry’s law:

\[
p_i = c_i H_i
\]

in which \( p_i [\text{Pa}] \) is the partial pressure of compound \( i \). Assuming ideal gas behavior, the concentrations \( c_i^g [\text{mol/m}^3] \) in the gaseous phase are related to the respective partial pressures by:

\[
c_i^g = \frac{p_i}{RT}.
\]

If a gaseous phase is present, the sum of all partial pressures must equal the gaseous-phase pressure \( p [\text{Pa}] \). If no gaseous phase is present, the sum of partial pressures computed through Henry’s law is smaller than \( p \):

\[
\sum_{i=1}^{N} \left\{ \begin{array}{ll} p & \text{if } S_i > 0 \\ < p & \text{if } S_i = 0 \end{array} \right.
\]

in which \( N \) is the number of volatile compounds. The gaseous-phase pressure \( p \) is the sum of the aqueous-phase pressure \( p_a \) and the capillary pressure \( p_c \). The value of \( p \) is at least the atmospheric pressure of \( \approx 10^5 \) Pa, whereas the capillary pressure \( p_c \) depends
on the surface tension $\sigma = 7 \cdot 10^{-2}$ N/m of water and the radius of the entrapped gas bubbles $r$ [m] by $p_c = 2\sigma/r$ (Atkins, 1997). For a radius $r$ of $10^{-4}$ m, the capillary pressure $p_c$ is at the order of $10^3$ Pa and its contribution to $p$ is relatively small. In the following analysis, we will neglect the dependency of $p$ on $S_g$. If the flow is horizontal and the total head drop is small, we can assume $p$ approximately constant.

As long as a gaseous phase is present, the total pressure of all volatile compounds is given. By changing the composition of the solutes, as will be seen later, we may change the gas saturation $S_g$ and therefore the partitioning behavior of all volatile compounds. This implies non-linear mass-transfer of the mixture, even though for each compound the partial pressure in the gas phase is proportional to the concentration in the aqueous phase, according to Henry's law (Eq. (4)). The volatile compounds compete for "space" within the gaseous phase, in the sense that the sum of the partial pressures is fixed. Given certain total amounts of volatile compounds per pore volume, the gas saturation $S_g$ and the aqueous phase concentrations $c_i$ will adapt so that Eq. (6) and Henry's law (Eq. (4)) are satisfied.

The mixture of volatile compounds is not determined solely by the aqueous-phase concentrations $c_i$ but also depends on the gas saturation $S_g$. The analysis is facilitated by using the total concentration $C_i$ of each compound $i$, defined as the mass in all phases per pore volume (Helfferich, 1981):

$$C_i = (1 - S_g)c_i + S_g c_i^g = \left(1 + \left[\frac{H}{RT} - 1\right]S_g\right)c_i.$$  \hspace{1cm} (7)

We can express the partial pressure $p_i$ as function of the total concentration $C_i$ by:

$$p_i = \frac{C_i H_i}{1 + \left(\frac{H_i}{RT} - 1\right)S_g}.$$  \hspace{1cm} (8)

Given $C_i$ of all compounds, the gas saturation $S_g$ can be evaluated by the following approach: (1) Evaluate the nominal gas pressure $\bar{p}$ for $S_g = 0$:

$$\bar{p} = \sum_{i=1}^{N} C_i H_i.$$  \hspace{1cm} (9)

(2) If $\bar{p} < p$, no gaseous phase is present ($S_g = 0$), and $c_i^g = C_i$. (3) If $\bar{p} > p$, a gaseous phase is present, and $S_g$ must be determined by applying Eq. (8) and the condition that the sum of partial pressures is $p$. The analytical solution of the algebraic equation for a three- or more-component system is a lengthy expression, so that we prefer a numerical solution.

Applying Gibbs phase rule (Atkins, 1997), we can express one aqueous-phase concentration by all others and the gas saturation if a gaseous phase is present, whereas we need all aqueous-phase concentrations if no gaseous phase is present. By contrast, the total concentrations $C_i$ fully describe the composition independently of a gaseous phase being present. We assume that the compounds are advected in the aqueous phase,
and we neglect dispersive fluxes. Then, the mass flux vector \( F_i \) [mol/(m² s)] of
compound \( i \) is:

\[
F_i = q C_i = \frac{q C_i}{1 + \left( \frac{H_i}{\partial T} - 1 \right)} S_g
\]

(10)
in which \( q \) [m/s] is the volumetric flux or specific discharge vector of water. The
incompressibility condition for the water phase requires, for gradual changes in gas
saturation:

\[
\theta \frac{\partial S_g}{\partial t} - \nabla \cdot (q) = 0
\]

(11)
in which \( \theta \) [-] is the porosity assumed constant. Mass conservation of all compounds \( i \)
yields:

\[
\theta \frac{\partial C_i}{\partial t} + \nabla \cdot (F_i) = 0 \quad \forall \, i = 1, \ldots, N.
\]

(12)

The analysis that follows is restricted to one-dimensional domains. Then, \( q \) and \( F_i \)
are the scalar volumetric flux and mass flux of compound \( i \), respectively, and the
divergence \( \nabla \cdot (\cdot) \) simplifies to the spatial derivative, \( \partial / \partial x \), with respect to the spatial
coordinate \( x \) [m].

4. Numerical methods

Eqs. (11) and (12) are spatially discretized by integrated Finite Differences. An
operator-splitting approach is used for coupling flow, mass-transfer, and transport. Each
time step is divided into three sub-steps. Based on the change of gas saturation in all
cells during the preceding time step, the volumetric flux \( q \) at all interfaces is evaluated by
integration of Eq. (11). The resulting values of the volumetric flux \( q(x) \) and the gas
saturation from the previous gas-transfer calculations are substituted into Eq. (10) and
the corresponding fluxes \( F_i \) of all compounds \( i \) into Eq. (12) which is solved explicitly
using upstream differentiation. The time step is chosen so that a grid Courant number of
unity is reached for the fastest velocity observed in the domain. Based on the resulting
total concentrations \( C_i \), the nominal gas pressure \( \bar{p} \) according to Eq. (9) is evaluated in
every cell. If \( \bar{p} > p \), the gas saturation \( S_g \) and the partial pressures \( p_i \) satisfying Eqs. (6)
and (8) are evaluated by a Newton–Raphson scheme. Evaporation of water is neglected in
the pressure calculations, since the vapor pressure of water is only about 1% of the
atmospheric pressure under standard conditions. Finally, the rate of saturation change
\( \partial S_g / \partial t \approx \Delta S_g / \Delta t \) are calculated for all cells. The aqueous-phase concentrations \( c \),
corresponding to \( C_i \) and \( S_g \) are evaluated from Eq. (7).

The operator-splitting approach introduces an error that acts like mass-transfer
kinetics because it delays the mass exchange. Upstream differentiation causes numerical
dispersion. Both numerical errors lead to smoothed concentration profiles. These effects
are minor because the system itself leads to self-sharpening of fronts; nonetheless, they are further reduced by choosing a very fine spatial discretization of 1000 cells. The CPU time required for simulating a Heaviside problem with three compounds over a time period of 45 pore volumes is slightly less than 2 min on a PC with a Pentium III 500 MHz processor operating under Linux.

5. Analysis of coherent waves

For a system with \( N \) volatile compounds, we have formulated \( N+1 \) partial differential equations, Eqs. (11) and (12). Due to the total-pressure constraint (Eq. (6)), however, there are only \( N \) degrees of freedom. In the following, we will substitute the continuity equation (Eq. (11)) into the \( N \) transport equations (Eq. (12)) and eliminate the gas saturation \( S_g \) from the list of unknowns. The resulting system of hyperbolic equations is then decomposed into its characteristic components. Any variation of the composition of volatile compounds will be split up into its characteristic components each propagated with its characteristic velocity. We will first analyze smooth variations, followed by considerations of discontinuities that may result from boundary conditions or the wave propagation itself.

5.1. Propagation of smooth variations

Differentiating the mass flux, Eq. (10), considering Eq. (11), and substituting the resulting expressions into Eq. (12) gives:

\[
\theta \frac{\partial C_i}{\partial t} + q \frac{\partial C_i}{\partial x} + c_i \theta \frac{\partial S_g}{\partial t} = 0.
\]

(13)

Next, substitute \( c_i \) in terms of \( C_i \) and \( S_g \):

\[
\theta \frac{\partial C_i}{\partial t} + q \left( \frac{\partial C_i}{\partial C_i} \frac{\partial C_i}{\partial x} + \frac{\partial c_i}{\partial S_g} \frac{\partial S_g}{\partial x} \right) + \frac{\theta C_i}{1 + \left( \frac{H_i}{R T} - 1 \right) S_g} \frac{\partial S_g}{\partial t} = 0
\]

(14)

with

\[
\frac{\partial c_i}{\partial C_i} = \frac{1}{1 + \left( \frac{H_i}{R T} - 1 \right) S_g}
\]

(15)

\[
\frac{\partial c_i}{\partial S_g} = - \frac{C_i \left( \frac{H_i}{R T} - 1 \right)}{\left( 1 + \left( \frac{H_i}{R T} - 1 \right) S_g \right)^2}.
\]

(16)
Substitution of Eqs. (15) and (16) into Eq. (14) yields:

\[
\left(1 + \left(\frac{H_i}{\frac{\partial R}{\partial T} - 1}\right)S_g\right) \frac{\partial C_i}{\partial t} + C_i \frac{\partial S_g}{\partial t} + \frac{q}{\theta} \frac{\partial C_i}{\partial x} - \frac{q C_i \left(\frac{H_i}{\frac{\partial R}{\partial T} - 1}\right)}{\theta \left(1 + \left(\frac{H_i}{\frac{\partial R}{\partial T} - 1}\right)S_g\right)} \frac{\partial S_g}{\partial x} = 0.
\]

Equation

\[
\sum_{j=1}^{N} \frac{C_j H_j}{1 + \left(\frac{H_j}{\frac{\partial R}{\partial T} - 1}\right)S_g} = \rho
\]  (18)

implicitly defines \( S_g \) as a function of \( C_1, \ldots, C_N \). We may now substitute the time and space derivatives of \( S_g \) by the sum of those of all total concentrations \( C_j \):

\[
\left(1 + \left(\frac{H_i}{\frac{\partial R}{\partial T} - 1}\right)S_g\right) \frac{\partial C_i}{\partial t} + C_i \sum_{j=1}^{N} \frac{\partial S_g \partial C_j}{\partial C_j} + \frac{q}{\theta} \frac{\partial C_i}{\partial x} - \frac{q C_i \left(\frac{H_i}{\frac{\partial R}{\partial T} - 1}\right)}{\theta \left(1 + \left(\frac{H_i}{\frac{\partial R}{\partial T} - 1}\right)S_g\right)} \sum_{j=1}^{N} \frac{\partial S_g \partial C_j}{\partial C_j} = 0
\]  (19)

in which \( \partial S_g / \partial C_i \) may be evaluated using Eq. (18) either analytically or through numerical differentiation. Eq. (19) can be written in matrix form:

\[
A \frac{\partial \mathbf{C}}{\partial t} + B \frac{\partial \mathbf{C}}{\partial x} = 0
\]  (20)

in which \( \mathbf{C} \) is the vector of the total concentrations \( C_j \) of all compounds, and the entries of the matrices \( A \) and \( B \) are given by:

\[
A_{ij} = \left(1 + \left(\frac{H_i}{\frac{\partial R}{\partial T} - 1}\right)S_g\right) \delta_{ij} + C_i \frac{\partial S_g}{\partial C_j}
\]  (21)

\[
B_{ij} = \frac{q}{\theta} \left(\delta_{ij} - \frac{C_j \left(\frac{H_j}{\frac{\partial R}{\partial T} - 1}\right)}{1 + \left(\frac{H_j}{\frac{\partial R}{\partial T} - 1}\right)S_g} \frac{\partial S_g}{\partial C_j}\right)
\]  (22)

Matrices \( A \) and \( B \) are diagonal only in the limiting case of \( S_g \) constant in space and time. In this special case, the volatile compounds are advected independently, each with its own retardation coefficient and thus the linear theory of partitioning tracers is valid. In general, however, a change in the composition will be associated with a change in gas saturation, particularly because the compounds are retarded differently. The change in
gas saturation is negligible for all practical purposes when concentration changes in the aqueous phase are very small. This was not the case in the experiments of Fry et al. (1995, 1996), Donaldson et al. (1997, 1998), and Hofmann (1996).

Eq. (20) is then transformed into its characteristic system:

\[
\frac{\partial \mathbf{C}}{\partial t} + \mathbf{A}^{-1} \mathbf{B} \frac{\partial \mathbf{C}}{\partial x} = 0
\]

\[
\mathbf{E}^{-1} \frac{\partial \mathbf{C}}{\partial t} + \Lambda \mathbf{E}^{-1} \frac{\partial \mathbf{C}}{\partial x} = 0
\]

(23)

(24)

where \( \mathbf{B} = \mathbf{E} \mathbf{A} \mathbf{E}^{-1}, \) \( \Lambda \) is the diagonal matrix of the eigenvalues of \( \mathbf{B} \), and the column-vectors \( \mathbf{e}_i \) of matrix \( \mathbf{E} \) are the eigenvectors of \( \mathbf{B} \). The eigenvector \( \mathbf{e}_i \) corresponds to the \( i \)th eigenvalue \( \lambda_i \). Next, we may introduce the vector of characteristic variables \( \mathbf{u} \) satisfying:

\[
\frac{\partial \mathbf{u}}{\partial t} = \mathbf{E}^{-1}.
\]

(25)

Then, Eq. (24) can be expressed in terms of \( \mathbf{u} \) rather than \( \mathbf{C} \):

\[
\frac{\partial \mathbf{u}}{\partial t} + \Lambda \frac{\partial \mathbf{u}}{\partial x} = 0.
\]

(26)

Eq. (26) is a system of \( N \) uncoupled first-order hyperbolic equations each of which can be expressed in its characteristic form:

\[
\frac{du_i}{dt} = 0 \quad \text{along} \quad \frac{dx}{dt} = \lambda_i.
\]

(27)

We may express a small variation \( \delta \mathbf{C} \) of the total concentrations \( \mathbf{C} \) as a sum of \( d_i \)-components, where \( d_i = (\langle \mathbf{e}_i \cdot \delta \mathbf{C} \rangle/\|\mathbf{e}_i\|^2)\mathbf{e}_i \), each traveling through the domain with its characteristic velocity \( \lambda_i \). That is, in general, a variation \( \delta \mathbf{C} \) will be split into \( N \) waves. The system is non-linear, i.e., matrices \( \mathbf{A} \) and \( \mathbf{B} \) depend on the vector of total concentrations \( \mathbf{C} \), so that the characteristic speed \( \lambda_i \) varies with \( \mathbf{C} \). We can distinguish between three cases of spatial variability of \( \lambda_i \): if the characteristic velocity increases in the direction of propagation, the wave is referred to as rarefaction wave; if it decreases, the wave is self-sharpening; and if it remains constant, the wave is indifferent (Whitham, 1974; Hefferich and Carr, 1993). In the system of interest, the characteristic speeds \( \lambda_i \) are associated with the gas saturation \( S_g \). That is, a wave is self-sharpening if \( S_g \) increases with the direction of flow, because all compounds are retarded more strongly at the downstream side of the variation than at the upstream one. Conversely, a rarefaction wave will be observed if \( S_g \) decreases in the direction of flow. Self-sharpening waves may result in the formation of shocks, that is, moving discontinuities, even if the initial variation is smooth.

It should be noted that for the case in which a gaseous phase is present (\( S_g > 0 \)) at both sides of the variation, one eigenvalue \( \lambda_i \) will be zero and only \( N - 1 \) waves are propagated through the domain. We can explain this behavior by the total-pressure
constraint, Eq. (6). Eq. (13) may be transformed by substituting the aqueous-phase concentration $c_i$ by the partial pressure $p_i$:

$$\frac{\partial C_i}{\partial t} + \frac{q}{\theta} \frac{\partial p_i}{\partial x} + p_i \frac{\partial \xi}{\partial t} = 0. \quad (28)$$

Summing over all compounds and accounting for Eq. (6) yields:

$$\sum_{i=1}^{N} H_i \frac{\partial C_i}{\partial t} + \frac{q}{\theta} \frac{\partial p_i}{\partial x} + p \frac{\partial \xi}{\partial t} = 0 \quad (29)$$

$$\sum_{i=1}^{N} \left( H_i + p \frac{\partial \xi}{\partial C_i} \right) \frac{\partial C_i}{\partial t} = 0. \quad (30)$$

Hence, provided that a gaseous phase remains present, one eigenvector $e_i$ consists of components that are inversely proportional to $H_i + p(\partial \xi/(\partial C_i))$, and its eigenvalue is zero. A wave that is not propagated through the domain is referred to as a standing wave. The significance of the standing wave can be explained more easily in the context of discontinuous distributions, which are discussed in the following section.

5.2. Shock waves and semi-analytical solution of Riemann and Hewiside problems

At discontinuities, spatial derivatives are not defined and Eq. (26) is not valid. However, we can enforce conservation of water and all compounds across the discontinuity. Consider the $k$th wave to be associated with a jump in the total concentrations. The velocity of this wave is $v_k$, which, for convenience, is assumed positive. Then, mass conservation yields:

$$q_k - q_{k-1} + \theta v_k (S_k - S_{k-1}) = 0 \quad (31)$$

$$F_i^k - F_i^{k-1} - v_k \theta (C_i^k - C_i^{k-1}) = 0 \quad (32)$$

in which the indices $k-1$ and $k$ for $q$, $S$, $F$ and $C_i$ denote the states upstream and downstream of the discontinuity. In a coherent wave, the concentration jumps of all compounds $i$ are propagated with identical velocity $v_k$, which is equivalent to the characteristic velocity $\lambda_k$ discussed for the case of smooth variations. Substituting Eq. (10) into Eq. (32) yields for all compounds $i$:

$$v_k = \frac{\left( \frac{q_k C_i^k}{\theta \left( 1 + \left( \frac{H_i}{\beta T} - 1 \right) S_k \right)} - \frac{q_{k-1} C_i^{k-1}}{\theta \left( 1 + \left( \frac{H_i}{\beta T} - 1 \right) S_{k-1} \right)} \right)}{C_i^k - C_i^{k-1}}. \quad (33)$$
We may use Eq. (33) for solving a Riemann problem, which is the transport problem associated with a single discontinuity of the total concentrations $C_i$ in an infinite domain. The initial condition is:

$$ C_i(x_0, x) = \begin{cases} 
C_i^- & \text{if } x \in [\infty, x_0] \\
C_i^+ & \text{if } x \in [x_0, +\infty] 
\end{cases} \quad (34) $$

in which the superscripts $-$ and $+$ denote the left hand and right hand-side values at the initial time $t_0$, and $x_0$ is the spatial coordinate of the discontinuity. An approximate solution is given by assuming that all waves associated with the initial jump are shock waves. Then, the solution consists of $N$ joint discontinuities of all compounds propagated with velocities $v_k$. Between the passing of two shocks, the concentrations are constant. Under this assumption, Eq. (33) can be formulated for all compounds $i$ and all waves $k$. This gives a set of $N^2$ equations.

The problem is solvable if, beside $C_i^-$ and $C_i^+$, the ratio $q/\theta$ upstream of the slowest wave is given. Obviously, $C_i^0 = C_i^-$ and $C_i^N = C_i^+$. The unknowns we seek for are the total concentrations of all compounds at the intermediate states $C_i^1, C_i^2, \ldots, C_i^{N-1}$ and all shock velocities $v_k$. The resulting system of $N^2$ non-linear equations may have multiple solutions. Only in one solution, however, the shock velocities $v_k$ increase with $k$.

In case of total dissolution of the gaseous phase ($S^- = 0$ and $S^+ > 0$), the slowest velocity $v_1$ is associated with the dissolution of the gaseous phase. We can determine the velocity $v_1$ by considering transport of the sum of partial pressures. The wave associated with the change of the sum of partial pressures is the dissolution front. We rewrite the balance Eqs. (31) and (32) considering the states $C^-$ and $C^+$ up- and downstream of the initial jump. We substitute the total concentrations $C_i$ by the partial pressures $p_i$ in Eq. (32) for all compounds and sum up the equations weighted by the corresponding Henry's law coefficient. Considering Eqs. (6) and (31), we arrive, after some rearrangements, at:

$$ v_1 = \frac{q^-}{\theta} \frac{p - \bar{p}^-}{p - \bar{p}^- + S^+ \sum_{i=1}^{n_i} \frac{H_i}{\bar{R}T}} \quad (35) $$

In order to determine the velocity of the dissolution front, we must know the volumetric flux $q^-$ and the total gas pressure $\bar{p}^-$ rather than all partial pressures upstream of the initial discontinuity, whereas the exact composition is needed at the downstream side.

In the case of a smooth variation, we have shown that there is one standing wave if a gaseous phase is present at both sides of the variation. This is also the case for a Riemann problem. Setting $v_1$ to zero in Eq. (31) yields that the specific discharge $q$ is identical at both sides of the standing wave and from Eq. (32) we get that the aqueous-phase concentrations must be identical, too. However, a jump in the gas saturation is possible. That is, if a gaseous phase is present at both sides of the initial discontinuity ($S^- > 0$ and $S^+ > 0$), we may observe a stagnant discontinuity of $S_i$ at $x_0$, even if the gas saturation was uniform at the initial state, and the aqueous-phase
concentrations around $x_0$ will be those of the upstream side at the initial state. Additionally $N-1$ traveling waves will evolve.

Once the approximate solution is found, we can test a posteriori whether indeed all waves are shock waves. We may evaluate matrices $\mathbf{A}$ and $\mathbf{B}$ according to Eqs. (21) and (22) for each concentration plateau and determine the eigenvalues of $\mathbf{B} = \mathbf{A}^{-1} \mathbf{B}$. The $k$th wave is a rarefaction wave if $k$th smallest eigenvalue of $\mathbf{B}$ is smaller for $\mathbf{C}^{k-1}$ than for $\mathbf{C}^k$. These eigenvalues are the velocities of the tail and the head of the rarefaction wave. In order to determine the exact shape of the wave, we need to evaluate the eigenvalue of consideration for all intermediate states between $\mathbf{C}^{k-1}$ and $\mathbf{C}^k$ (Helfferich and Curr, 1993). In the model calculation shown in Section 6, we have approximated the shape by simple linear interpolation between the tail and head of the wave.

Heaviside problems are based on a stepwise change of the flux entering a semi-infinite domain:

$$F_i^m = c_i^m q_i^m$$

(36)

in which $F_i^m$ is the mass flux of compound $i$ entering the domain, $c_i^m$ is the aqueous-phase concentration in the inflow differing from the uniform initial concentration $c_i^0$, and $q_i^m$ is the specific recharge. If the total gas pressure of the inflow $p^m = \Sigma H_i c_i^m$ is smaller than $p$, a gaseous phase cannot be sustained, and the semi-analytical solution is identical to the Riemann problem with $C^- = c_i^m$, $C^+ = c_i^0$, and $x_0 = x_m$. If $p^m = p$, the gaseous phase will not be dissolved, and $N-1$ traveling waves will evolve. In this case, the aqueous-phase concentrations upstream of the first traveling wave will be $c_i^m$, but the corresponding gas saturation $S_g$ is not known a priori. We can determine the upstream gas saturation, the velocities of the $N-1$ traveling waves, and the $N$ total concentrations at each of the $N-2$ intermediate levels by the $N(N-1)$ mass balance equations (Eq. (32)) at the traveling waves. Subsequently, we may correct for the shape of rarefaction waves as described for the Riemann problem.

6. Model calculations

In order to demonstrate the behavior of the system, we perform model calculations with boundary conditions similar to the experiment of Hofmann (1996). Two model approaches are used: numerical simulation of the governing pde's Eqs. (11) and (12) subject to local equilibrium of gas transfer, and the semi-analytical approach outlined in Section 5.2. We compare the temporal change of aqueous-phase concentrations and gas saturations downstream of an inflow boundary for three different gas tracers: SF$_6$, which was used in the experiment and has a Henry's law coefficient higher than nitrogen, 1,2-dichlorotetrafluoroethane (CFC-114) with a Henry's law coefficient between those of oxygen and nitrogen, and dichlorodifluoromethane (CFC-12) with a Henry's law coefficient smaller than that of oxygen. The physico-chemical properties of the compounds are listed in Table 1.

In all calculations, we assume a uniform distribution of the initial $S_g$ and $C$. For the initial gas saturation $S_g$ we assume a value of 0.25, $p$ is set to $10^3$ Pa, 80% of which is
contributed by nitrogen and 20% by oxygen. The temperature is 298 K. At the inflow boundary, a specific recharge $q_m$ and the aqueous-phase concentrations in the inflow $c_i^m$ of all compounds are given. In the first three applications, we simulate an experiment similar to that of Hofmann (1996). The partial pressures of the volatile compounds in the inflow are $2.4 \cdot 10^4$ Pa for nitrogen, $6 \cdot 10^3$ Pa for oxygen, and $3.5 \cdot 10^4$ Pa of a different tracer in each of the three applications. Like in the experiment, a Heaviside boundary condition is chosen. The sum of partial pressures in the inflow is smaller than the pressure $p$ so that a gaseous phase cannot be sustained. The parameters are chosen to fit the measured data shown in Fig. 1.

The following model results show the breakthrough curves of all volatile compounds, that is, the aqueous-phase concentrations $c_i$, and the gas saturation at the outflow end of the domain as function of dimensionless time $\tau$:

$$\tau = \frac{t \theta \bar{x}}{q_m}$$

in which $\bar{x}$ is the spatial coordinate of observation point which is at the end of the domain considered. In Figs. 2–7, the numerical model results are shown as bold lines, whereas the semi-analytical results are given as thin lines in Figs. 2–5. The concentrations and the gas saturation at the left-hand end of Figs. 2–7 are at the initial state, whereas the concentrations at the right-hand end are the injected concentrations and the corresponding gas-saturation is that reached in the entire domain after the new equilibrium is reached. The concentrations seen in the breakthrough curves could also be observed in a longitudinal profile at a time before the first wave arrives the end of the column.

Fig. 2 shows the modeled breakthrough curves and the gas saturation at the outflow end of the domain for the Heaviside problem using SF$_6$ as partitioning tracer. The
numeral and semi-analytical results are almost identical. Due to artificial dispersion, the numerical results show a slight smoothing of the sharp steps in the breakthrough curves. Three distinct shock waves can be observed. The first wave is mainly associated with a decrease in the concentrations of oxygen, the most mobile compound in the system considered. The gas saturation decreases slightly, nitrogen is enriched in the remaining gaseous phase, whereas SF$_6$ is not yet present. The second wave is associated with nitrogen depletion, a further decrease in gas saturation, and the SF$_6$ breakthrough. SF$_6$ is highly enriched in the gaseous phase. The third wave is the dissolution front traveling with the velocity given by Eq. (35). Upstream of this wave, no gaseous phase is present and the concentrations equal those in the inflow. In this regime, no compound is retarded and the effective velocities of all compounds are maximal. Here, SF$_6$ injected with the inflow travels much faster than the dissolution front explaining the strong SF$_6$ enrichment.

Fig. 2 includes the SF$_6$ concentration measurements at the outflow of the experimental column (Hofmann, 1996). Note that only relative concentration values were measured, so that the concentrations in Fig. 2 are scaled by an assumed inflow concentration. The inflow concentration of SF$_6$ and the initial gas saturation $S_g$ are manually fitted to meet the concentration plateaus and the times of the two distinct concentration changes. Notwithstanding the delayed response of the measured concentrations due to kinetic gas transfer and the possible smoothing due to dispersion, the breakthrough curve
of SF₆ in the model calculations is qualitatively similar to that of the experiment. Obviously, the experimental setup was not appropriate to determine the saturation of the immobile gas. According to our model, the gaseous phase was completely dissolved during the experiment. The tracer did not behave according to Eqs. (2) and (3). Had S₉ been 0.25 all the time, the breakthrough of SF₆ would have occurred at τ = 57.6. The stepwise dissolution of the gaseous phase led to an earlier breakthrough, and the non-linear interaction with other volatile compounds to an enrichment of the tracer in the gaseous phase. The enrichment cannot be explained with a model based on constant gas saturation. Neither mass-transfer kinetics nor dispersion would lead to such a behavior.

Fig. 3 shows the modeled breakthrough curves and the gas saturation at the outflow end of the domain for the Heaviside problem injecting CFC-114 rather than SF₆. Again, three waves can be observed. The first wave, mainly associated with oxygen depletion, is practically identical to that of the SF₆ test shown in Fig. 2. Also the breakthrough time of the third wave, associated with the dissolution of the gaseous phase, is identical because the velocity of the dissolution depends on the total gas pressure in the inflow regardless of the partial pressures (Eq. (35)). The first and third waves are shock waves. In contrast to the previous application, the second wave is a rarefaction wave. The Henry’s law coefficient of CFC-114 is smaller than that of nitrogen, so that the tracer is more mobile. As a consequence, the gas saturation increases with the second wave, and

![Graph](image-url)

**Fig. 3.** Modeled aqueous-phase concentrations and gas saturation at the outflow and of the domain as function of dimensionless time due to stepwise introduction of 1,2-dichlorotetrafluoroethane (CFC-114).
all volatile compounds are retarded more strongly upstream than downstream of the wave. Note that the linear approximation of the rarefaction wave in the semi-analytical approach is in excellent agreement with the numerical model results. As in the case of SF₆ injection, the gas tracer is highly enriched before complete dissolution of the gaseous phase.

Fig. 4 shows the modeled breakthrough curves and the gas saturation at the outflow end of the domain for the Heaviside problem injecting CFC-12. The Henry’s law coefficient of CFC-12 is smaller than that of oxygen. As a consequence, the tracer breakthrough dominates the first wave. Associated with the first wave is an increase of the gas saturation, so that a rarefaction wave can be observed. The two following waves, associated with oxygen depletion and total dissolution of the gaseous phase, are shock waves. After passing of the first wave, the gas saturation reaches a value of \( \approx 0.35 \), which means that the gaseous phase might become mobile, a possibility that is not covered by our model. Intuitively, one would not expect to mobilize trapped gas by injection of a solution in which the sum of partial pressures is significantly smaller than the pressure of the fluid. Since the volatility of the injected compound is much lower than those of nitrogen and oxygen, we observe first an increase of volatile compounds followed by the complete dissolution of the gaseous phase.

A common feature of the three applications discussed so far is that the volatile compounds in the injected water cannot sustain a gaseous phase. Next, we present

![Fig. 4. Modeled aqueous-phase concentrations and gas saturation at the outflow end of the domain as function of dimensionless time due to stepwise introduction of dichlorodifluoromethane (CFC-12).](image)
results where the total gas pressure $\bar{p}$ in the injected water equals the gaseous-phase pressure $p$ so that the gaseous phase is not totally dissolved by the tracer test. We consider CFC-12 as tracer introduced as pulse contributing 35% of $\bar{p}$, the remaining 65% being distributed in a ratio of 4:1 between nitrogen and oxygen. The initial conditions are identical to those in the previous calculations. Fig. 5 shows the breakthrough curve caused by a long pulse where the waves associated with start and end of tracer injection do not interfere, whereas Figs. 6 and 7 show results of short pulses where the waves of the second discontinuity already interact with those of the first. The dimensionless injection times are 10, 3, and 0.3 pore volumes for Figs. 5, 6, and 7, respectively.

Fig. 5 shows the modeled breakthrough curves and the gas saturation at the outflow end of the domain for a long pulse of CFC-12 sustaining the existence of an immobile gaseous phase. Each change of inflow concentration splits up into two traveling waves. Since CFC-12 is more mobile than oxygen and nitrogen, the gaseous-phase saturation increases during the injection resulting in two rarefaction waves associated with the start of the tracer injection, and in two shock waves associated with the end of tracer injection. Both the concentrations and the gaseous-phase saturation are identical before the start of the injection and after all waves have passed through. This would not be the case if the gaseous phase were completely dissolved, since the formation of a gaseous

![Graph showing modeled concentrations and gas saturation](image-url)

Fig. 5. Modeled aqueous-phase concentrations and gas saturation at the outflow end of the domain as function of dimensionless time in response to a pulse of dichlorodifluoromethane (CFC-12) sustaining the existence of an immobile gaseous phase. Pulse length 10 pore volumes.
phase in a water-saturated medium can be enforced only by injection of a solution that is
oversaturated with gaseous compounds ($\bar{p} > p$).

The first wave corresponding to the end of tracer injection travels faster than the
second wave, of the start of injection. Hence, if we decrease the duration of pulse
injection or observe a point further downstream, these waves interfere. In this study, we
have not developed analytical results for interfering waves. Numerical model results are
shown in Fig. 6 for a pulse of 3 pore volumes, and Fig. 7 for 0.3 pore volumes.
According to Helfferich and Whitley (1996), the sharpening behavior of interfering
waves is not altered. In Fig. 6, the second rarefaction wave has been surpassed by the
third shock wave, and the resulting pattern is a rarefaction and shock wave bounding the
tracer pulse followed by a rarefaction and shock wave bounding a variation in the
oxygen/nitrogen ratio. While the tracer pulse is rather sharp except for some fronting, it
is related with a significantly higher saturation of the gaseous phase. By further reducing
the dimensionless pulse size, shown in Fig. 7, the shock wave associated with the tracer
decrease also surpasses the tail of the rarefaction wave associated with the increase. As a
consequence, we can no more observe a plateau of the tracer concentration. By contrast,
the head of the first wave in Figs. 6 and 7 is not affected by the waves associated with
the end of tracer injection. Therefore, the shape of this head is identical in the two
figures.

![Graph](image)

Fig. 6. Modeled aqueous-phase concentrations and gas saturation at the outflow end of the domain as function of dimensionless time in response to a pulse of dichlorodifluoromethane (CFC-12) sustaining the existence of an immobile gaseous phase. Pulse length 3 pore volumes.
In the case of the shortest pulse, Fig. 7, the fronting of the tracer breakthrough curve creates a remarkably high amount of spreading. The fronting is caused by the continuous increase of the gas saturation and not by dispersion or kinetic mass-transfer. Including the latter processes in the simulations would cause further smoothing of the breakthrough curve.

7. Discussion and conclusions

Determining the saturation of a trapped gas phase by a partitioning-tracer test may be more complex than anticipated from linear theory of partitioning tracers and Henry's law, Eqs. (2) and (3), at least when high tracer concentrations are used. The tracer test is based on changing the composition of the volatile compounds in the aqueous solution. By adding a tracer into the injected solution, the concentrations of the compounds already present in the porous medium must be decreased, because the sum of partial pressures cannot exceed the hydrostatic pressure of the gaseous phase in the medium. That is, in an aerobic aquifer without major microbial activity, at least three concentration changes are to be considered: those of the tracer, nitrogen and oxygen.

The specific velocities of the volatile compounds are different, because each compound has its own Henry's law coefficient. Assume for a moment that the linear theory
of partitioning tracers was applicable. Then, if the gas tracer is less volatile than oxygen and nitrogen, such as in the case of CFC-12, an observer downstream of the injection point would first experience the increase of the tracer concentration and then the decrease of oxygen and finally nitrogen. If the volatilicity of the tracer is between those of oxygen and nitrogen, such as in the case of CFC-114, the simplified pattern would consist of a decrease of oxygen, followed by an increase of the tracer and a decrease of nitrogen. Finally, a very volatile tracer such as SF₆ would cause a pattern of oxygen and nitrogen concentration decreases followed by the increase of the tracer.

Obviously, these simple patterns, predicted by linear theory of partitioning tracers, can be observed only partially. The system behaves differently because, provided that a gaseous phase is present, the sum of partial pressures is fixed. Consider the case where we inject a rather mobile tracer such as CFC-12 (see Fig. 4). Then, the increase of the tracer concentration, anticipated from linear theory of partitioning tracers as the first response to the start of injection, must be accompanied with a decrease of the other compounds, so that the sum of partial pressures remains constant. The system, moreover, can adapt to the increased input of the tracer by increasing the gas saturation. The two waves that would be associated with the decrease of oxygen and nitrogen in the linear theory of partitioning tracers are also modified to traveling changes of all concentrations and the gas saturation. Similar patterns can be observed for the other tracers.

By changing the gas saturation, the retardation of all volatile compounds is also changed. If the gas saturation is smaller at the upstream than at the downstream side of a wave, all compounds are transported faster at the upstream side, and the wave is self-sharpening. By contrast, the wave tends to spread if the gas saturation at the upstream side of a wave is higher than at the downstream side.

We have analyzed the transport of volatile compounds in the presence of a trapped gas phase by the coherence theory which is known as an effective tool in the analysis of multi-component multi-phase systems (Helfferich, 1981; Helfferich and Whitley, 1996). Our analysis shows which combinations of concentration variations are propagated jointly through the domain and at which celerity. For the case of shock waves, the system simplifies to algebraic conservation laws at moving discontinuities. The resulting system of non-linear algebraic equations can be solved with standard solvers included in commercial spreadsheet software such as Microsoft Excel. Our model calculations show excellent agreement between numerical model results and the semi-analytical solutions. Given the computational power available today, the purpose of such semi-analytical solutions is not to save computation time but to give insight in the development of plateaus, waves and their sharpening or non-sharpening behavior. E.g., the enrichment of the gas tracer in the experiment shown in Fig. 1 can be explained with wave theory. Similar behavior is known, and explained by coherence theory, for competitive sorption in chromatography and ion exchange (Helfferich and Whitley, 1996).

In our analysis, we have neglected dispersive transport and mass-transfer kinetics. These simplifications are reasonable if the characteristic time of advection is much larger than that of mass-transfer and much smaller than that of dispersion. For given velocity, mass-transfer and dispersion coefficients, these conditions will be met at an observation point that is far downstream of the injection point. In general, both of the
neglected processes smooth the breakthrough curves, and shock waves are modified to continuous traveling waves. Fig. 1 indicates that either kinetic mass-transfer or dispersion were significant in the SF₆-injection experiment, since both the increase and decrease of the SF₆-concentration were not abrupt as in the model results shown in Fig. 2. The model derived in the present study, however, gives the correct plateau concentrations, mean travel times and sharpening behavior of the waves. Analytical expressions for the large-time shapes of the waves considering mass-transfer kinetics and dispersion might be developed following the approach of van der Zee (1990) for non-equilibrium adsorption. Numerical models may follow the line of Donaldson (1997, 1998). Such derivations, however, are beyond the scope of the present study.

Our model may be used to design partitioning tracer-tests for quantifying the saturation of a trapped gas phase. Obviously, it is important to minimize the impact of the tracer test on the gas saturation itself. This might be done by adding an extremely small amount of the volatile tracer to a solution that is at equilibrium with the gas to be quantified. For systems in which the immobile gas is compositionally identical to atmospheric air, such as in the experiment of Hofmann (1996), this could be achieved fairly easily. In many field applications, however, the composition of the immobile gaseous phase has been significantly altered by oxygen depletion, volatilization of contaminants, or microbial production of gaseous compounds. In such cases, standard handling of extracted groundwater might change the composition of volatile compounds and re-injection of the extracted water would lead to the development of fronts analyzed in the present study, even without adding a volatile compound as tracer.

Acknowledgements

This study was made possible by a research scholarship of the Deutsche Forschungsgemeinschaft under the grant Ci 26/3-1. We are grateful for the provision of the experimental data by Reinhold Josef at the Universität Stuttgart. We thank two anonymous reviewers for their constructive remarks in improving the paper.

References


