Assessment of interfacial mass transfer in water-unsaturated soils during vapor extraction

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Abstract

This paper presents results of a numerical investigation of soil vapor extraction (SVE) systems at the laboratory scale. The SVE technique is used to remove volatile chlorinated hydrocarbons (VCHC) from the water-unsaturated soil zone. The developed numerical model solves equations of flow, transport and interfacial mass transfer regarding an isothermal $n$-component and three-phase system. The mathematical model is based on a simple pore network and phase distribution model and designed to be scaled by a characteristic length. All mathematical expressions are structured into VCHC specific and VCHC non-specific parameters. Furthermore, indicators are introduced that help to separate thermodynamic equilibrium from thermodynamic non-equilibrium domains and to determine the controlling physical parameters.

For numerical solution, the system of partial differential equations is discretized by a finite volume method and an implicit Euler time stepping scheme. Computational effort is reduced notably through techniques that enable spatial and temporal adaptivity, through a standard multigrid method as well as through a problem-oriented sparse-matrix storage concept.

Computations are carried out in two dimensions regarding the laboratory experiment of Fischer et al. [Water Resour. Res. 32 (12) 1996 3413]. By varying the characteristic length scale of the pore network and phase distribution model, it is shown that the experimental gas phase concentrations cannot be explained only by the volatility and diffusivity of the VCHC. The computational results suggest a sorption process whose significance grows with the aqueous activity of the less or non-polar organic compounds.

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1. Introduction

Soil vapor extraction (SVE), also known as soil venting, is the standard in-situ clean-up technique targeting the removal of volatile chlorinated hydrocarbons (VCHC) from the water unsaturated soil zone: An induced gas flow towards vertical or horizontal wells causes the evaporation of the non-aqueous phase liquid (NAPL), the volatilization of the contaminants dissolved in soil water and the desorption of the contaminants from the solid particles.

While the technical implementation of the SVE method is comparatively simple, its success depends on controlling complex physical, chemical and biological processes and requires insight into factors limiting its performance.

Various numerical and experimental investigations indicate that removal efficiency can be constrained by rate-limiting interfacial mass transfer especially during the evaporation of the residual NAPL (Ng and Mei, 1999), the volatilization of the contaminants dissolved in soil water (Armstrong et al., 1994; Fischer et al., 1996) and during the desorption of the contaminants from the soil particles (Ball and Roberts, 1991; Brusseau, 1991; Pavlostathis and Mathavan, 1992; Gierke et al., 1992; Morrissey and Grismer, 1999).

Though these kinetic effects are well known and generally accepted in science, their thorough quantification remains still not satisfactorily managed in systems of two or three interacting phases. On the one hand various authors (Welty et al., 1984; Roberts et al., 1985; Szatkowski et al., 1994; Schlünder, 1996) emphasize the importance of geometrical parameters like phase distributions, diffusion lengths or interfacial areas. Those govern essentially interfacial mass transfer kinetics, but they are difficult to estimate by averaging techniques (Hassanizadeh and Gray, 1979; Bear and Bachmat, 1986) or to measure via laboratory experiments (Silverstein and Fort, 1997; Anwar et al., 2000). This study tries to capture the scale of geometric constraints through finding a characteristic length, say the grain diameter $d_k$, of a simplified but physically consistent pore network and phase distribution model. A similar approach has recently been presented by Ng and Mei (1999). They idealized microscopic fluid distributions to model multicomponent vapor transport in a SVE system and demonstrated how this idealization can help to explain and predict intricate phenomena from basic principles.

On the other hand, the highly specific behavior of VCHC with regard to diffusion, volatilization and sorption does not provide any simple rule for an assessment of VCHC interfacial mass transfer in a system of several immobile or mobile phases. Therefore, a comparatively detailed mathematical model is developed that is structured into VCHC specific parameters (like diffusion coefficients or aqueous activity coefficients) and VCHC non-specific parameters (like diffusion lengths or interfacial areas). On the basis of this a dimensionless consideration of the physical system is performed, leading to thermodynamic equilibrium indicators that rely on rigorous mass balance constraints. Those enable us to compare thermodynamic states of chemical compounds in different phases to each other and, in particular, to identify those physical parameters that control the mass transfer kinetics and explain the consequences for the VCHC specific mass flux. Thermodynamic equilibrium indicators have been developed for kinetic gas–liquid mass transfer by Fischer et al. (1998) and liquid–solid mass transfer by Kaleris and Croisé (1997). So far, geometrical constraints have not been considered explicitly for the separation of thermodynamic states.
Furthermore, a two-dimensional laboratory test problem is investigated, leading to an accessory numerical model that solves implicitly two-dimensional flow, transport and interfacial mass transfer equations of an isothermal four-component and three-phase system. The numerical model is scaled and calibrated by two non-specific parameters, i.e. calibration is not carried out separately for each chemical compound. So far, this has not been successfully applied in any other two-dimensional SVE test problem.

2. Mathematical modeling

2.1. Main assumptions

We are concerned with the isothermal multicomponent gas flow in the water-unsaturated soil zone and with the interfacial mass transfer of the organic contaminants between the gas phase (g), the water phase (w) and the solid phase (s). The pure NAPL phase is not present. We neglect infiltration events and assume the water phase to be immobile in time, i.e. a stationary distribution of phase saturations. Furthermore, the gas phase is compressible, the water phase and the soil matrix are incompressible. On the macroscopic level, diffusive mass flux of contaminants in the water and the solid phase is neglected. Moreover, interfacial mass transfer between the gas phase and the soil matrix is not considered. This is valid as long as a wetting aqueous phase is present in the soil (Gierke et al., 1992; Thoma et al., 1999). The supply of oxygen into the contaminated area during the vapor extraction may promote co-metabolic degradation of less chlorinated hydrocarbons (Hopkins and McCarty, 1995; Bradley and Chapelle, 1998), however biodegradation processes are not considered.

2.2. Macroscopic mass balance equations

Regarding the assumptions we can write the following macroscopic mass balance equations for a two- or three-dimensional domain \( \Omega \). The mass balance for each component \( \kappa \) is:

\[
\phi S_g \rho_g \frac{\partial X^\kappa_g}{\partial t} + \phi S_w \rho_w \frac{\partial X^\kappa_w}{\partial t} + (1 - \phi) \rho_s \frac{\partial X^\kappa_s}{\partial t} + \nabla \cdot [\phi S_g (\rho_g X^\kappa_g v_g - F^\kappa_g)] = r^\kappa_g, \tag{1}
\]

with

\[
\phi S_w \rho_w \frac{\partial X^\kappa_w}{\partial t} = m^\kappa_{gw} - m^\kappa_{ws} \tag{2}
\]

and

\[
(1 - \phi) \rho_s \frac{\partial X^\kappa_s}{\partial t} = m^\kappa_{ws}. \tag{3}
\]
For the total mass we write
\[ \nabla \cdot (\phi S_g \rho_g v_g) = r_g, \]  
where the mass density of the gas phase is given by the ideal gas law:
\[ \rho_g = \frac{M_g p_g}{RT}. \]  
The following additional constraints have to be fulfilled:
\[ S_g + S_w = 1, \quad \sum_{\kappa=1}^{N} X_{\alpha}^{\kappa} = 1 \text{ for } \alpha \in \{g, w, s\}; \]  
where \( \phi \) is the porosity, \( S_g \) and \( S_w \) are the gas and water saturations, \( X_{\alpha}^{\kappa} \) is the mass fraction of component \( \kappa \) in phase \( \alpha \), \( v_g \) is the intrinsic velocity vector of the gas phase, \( F_{g}^{\alpha} \) is the hydrodynamic dispersive mass flux, \( r_g^{\kappa} \) is the specific mass generation of component \( \kappa \), \( m_{\alpha\beta}^{\kappa} \) is the specific mass transfer rate of component \( \kappa \) between the phases \( \alpha \) and \( \beta \), \( r_g \) is the total specific mass generation, \( p_g \) is the gas phase pressure, \( M_g \) is the molar mass of the gas phase, \( R \) is the ideal gas constant, \( T \) is the temperature.

2.3. Advective mass flux

The intrinsic velocity vector of the gas phase \( v_g \) can be estimated by Darcy’s law (homogenized Stokes equations; Tartar, 1980) assuming the gravity potential to be negligible:
\[ \phi S_g v_g = -\frac{k_r}{\mu_g} \nabla p_g, \]  
where \( k_r \) is the relative permeability, \( K \) is the intrinsic permeability tensor, \( \mu_g \) is the multicomponent gas viscosity calculated according to the method of Wilke (Bird et al., 1960; Reid et al., 1987). The necessary pure component gas viscosities can be estimated according to an alternate corresponding states relation of Reichenberg (Reid et al., 1987) for the low-pressure gas viscosity of organic compounds.

The relative gas permeability is assumed to be of the form (van Genuchten, 1980):
\[ k_{rg}^{\frac{1}{2}} = S_g^{\frac{1}{2}} (1 - (1 - S_g)^{\frac{1}{2}})^{2m}, \]  
where \( m \) is a van Genuchten parameter. After Fischer et al. (1996) and Dury et al. (1999) the effective gas saturation can be defined as
\[ S_g = \begin{cases} \frac{S_g - S_{ge}}{S_{ge} - S_{ge}} & : S_{ge} \leq S_g \leq S_{ge}, \\ 0 & : S_g < S_{ge} \end{cases}, \]  
where \( S_{ge} \) is the effective gas saturation.
where \( S_{g_e} \) is the emergence/extinction point (gas saturation at which gas flow emerges/extincts). \( S_{g_m} \) is the maximum possible gas saturation, also defined by

\[
S_{g_m} = 1 - S_{w_r},
\]

where \( S_{w_r} \) is the residual water saturation (water saturation that describes the transition between the coherent and incoherent phase distribution).

2.4. Hydrodynamic dispersive mass flux

The hydrodynamic dispersive mass flux for the gas phase is written as

\[
F^K_g = (D_g + D^K_g)(\rho_g \nabla X^K_g).
\]

Bear (1972) evaluates the mechanical dispersion tensor \( D_g \), which is valid for an isotropic medium, by:

\[
(D_g)_{ij} = \alpha_L \delta_{ij} \left| v_g \right| + (\alpha_L - \alpha_T) \frac{(v_{g_i})(v_{g_j})}{\left| v_g \right|},
\]

where \( \delta_{ij} \) is the Kronecker symbol, \( \alpha_L \) and \( \alpha_T \) are the longitudinal and transversal dispersitivities.

Assuming an isotropic medium and the pores to be approximate spheres, Millington (1959) estimates the effective gas molecular diffusion tensor to be

\[
D^K_g = \phi D^K_g S_g \tau \cdot I;
\]

where \( \tau = \phi^{1/3} S_g^{7/3} \) is a factor for the tortuosity and the multicomponent gas diffusion coefficient \( D^K_g \) can be calculated by Blanc’s law (Reid et al., 1987):

\[
D^K_g = \left( \sum_{l=1}^{n} \frac{x^l_g}{D_{l,K}} \right)^{-1},
\]

where \( x^l_g \) is the mole fraction of component \( l \), the pressure and temperature dependent binary gas diffusion coefficients \( D_{l,K} \) are estimated according to the method of Fuller (Reid et al., 1987).

2.5. Interfacial mass transfer

2.5.1. Two-film model

Interfacial mass transfer is described with the two-film model (Whitman, 1923; Bird et al., 1960; Welty et al., 1984; McCabe et al., 1993; Schlünder, 1996), which is applicable in
the case of stagnant or laminar flow conditions near the interfacial contact area. In this case, it can be assumed that the mass transfer between two phases is related to the diffusive fluxes across their interfacial viscous films. Setting the specific rate of mass transfer to the interface equal to the specific rate of mass transfer from the interface, it follows according to the linearized form of Fick’s first law that

\[
m_{\alpha \beta}^k = \frac{a_{\alpha \beta} D_{\alpha}^k}{l_{\alpha}} (\rho_{\alpha} X_{\alpha}^k - [\rho_{\alpha} X_{\alpha}^k]_{ph})
\]

and

\[
m_{\alpha \beta}^k = \frac{a_{\alpha \beta} D_{\beta}^k}{l_{\beta}} ([\rho_{\beta} X_{\beta}^k]_{ph} - \rho_{\beta} X_{\beta}^k),
\]

where \(a_{\alpha \beta}\) is the specific interfacial area between phase \(\alpha\) and \(\beta\), \(l_{\alpha}\) and \(l_{\beta}\) are the viscous film widths, \([\rho_{\alpha} X_{\alpha}^k]_{ph}\) and \([\rho_{\beta} X_{\beta}^k]_{ph}\) are the concentrations at the interfacial contact area.

The specific mass transfer rate can also be set equal to the product of an overall mass transfer rate coefficient \(\gamma_{\alpha \beta}^k\) with a measure for the thermodynamic non-equilibrium:

\[
m_{\alpha \beta}^k = \gamma_{\alpha \beta}^k (\rho_{\alpha} X_{\alpha}^k - [\rho_{\alpha} X_{\alpha}^k]_{eq});
\]

where \([\rho_{\alpha} X_{\alpha}^k]_{eq}\) is the fictitious \(\alpha\)-phase concentration in thermodynamic equilibrium with concentration \(\rho_{\beta} X_{\beta}^k\) in phase \(\beta\). Eq. (17) is related to Eqs. (15) and (16) by

\[
\frac{1}{\gamma_{\alpha \beta}^k} = \frac{1}{a_{\alpha \beta}} \left( \frac{l_{\alpha}}{D_{\alpha}^k} + \frac{l_{\beta}}{D_{\beta}^k} \left(\frac{[\rho_{\alpha} X_{\alpha}^k]_{ph} - [\rho_{\alpha} X_{\alpha}^k]_{eq}}{\rho_{\beta} X_{\beta}^k - \rho_{\beta} X_{\beta}^k}\right) \right).
\]

If thermodynamic equilibrium is assumed at the contact area between the viscous films, it follows that:

\[
\frac{1}{\gamma_{\alpha \beta}^k} = \frac{1}{a_{\alpha \beta}} \left( \frac{1}{\gamma_{\alpha}^k} + \frac{[\rho_{\alpha} X_{\alpha}^k]_{eq} - [\rho_{\alpha} X_{\alpha}^k]_{eq}}{\gamma_{\beta}^k ([\rho_{\beta} X_{\beta}^k]_{ph} - \rho_{\beta} X_{\beta}^k)} \right),
\]

where \(\gamma_{\alpha}^k = D_{\alpha}^k/l_{\alpha}\) and \(\gamma_{\beta}^k = D_{\beta}^k/l_{\beta}\) are the \(\alpha\)- and \(\beta\)-side mass transfer coefficients.

The viscous film widths can be more exactly quantified by expressions that result from a laminar boundary layer analysis, see, e.g. Friedlander (1957) and Bowman et al. (1961). On the basis of a Stokes flow, Quintard et al. (1997) discuss the validity of those expressions for an exemplary porous medium. In our study the gas phase represents the only mobile phase. It can be shown for low Reynolds numbers (< 1) that a decrease of the gaseous viscous film width, caused by an increase of the flow velocity, does not affect the gas–water mass transfer rate coefficient \(\gamma_{gw}\), since the gas-side mass transfer resistance is comparatively low (mind that the gaseous diffusion coefficients are four orders of magnitude larger than the aqueous diffusions coefficients, see Table 2). As we deal later with solid quartz grains as sorbent in which no intra-aggregate diffusion of VCHC occurs, the main resistance for interfacial mass transfer can be assumed in the aqueous phase. Furthermore, local heterogeneities regarding the spatial phase distribution are not
considered at all. Therefore, we set the focus rather on the scale of the viscous film widths than on their differences in single phases and assume near the interfacial contact area that \( l_\alpha \approx l_\beta \). Furthermore, we approximate the viscous film widths by the scale of a characteristic length, say the mean grain diameter \( d_k \):

\[
l_\alpha = l_\beta = d_k / 2.
\]

(20)

2.5.2. Specific interfacial area

We assume a simple pore network model, where the gas-filled pore space is approximated by a bundle of capillaries with diameter \( d_p \) and where the soil matrix is approximated by spherical grains with diameter \( d_k \) surrounded by the wetting aqueous phase (Fig. 1). If we assume for a unit flow cross-section an equal number of pores and grains, we find

\[
d_p = d_k \sqrt{\phi S_g / (1 - \phi)}.
\]

(21)

Since the hydraulic radius of a geometric body \( r_h \) is defined as the ratio of flow cross-section to wetted perimeter, we have for a single capillary

\[
r_h = d_p / 4,
\]

(22)

and for a unit volume

\[
r_h = \phi S_g / a_{gw},
\]

(23)

where \( a_{gw} \) is the specific interfacial area between the gas and the water phase. Eq. (23) is related to Eqs. (21) and (22) by the new expression

\[
a_{gw} = 4 \sqrt{\phi S_g (1 - \phi) / d_k}.
\]

(24)

Silverstein and Fort, 1997 show in their experiments a qualitative similar behavior of the interfacial area between the gas and the water phase. A decreasing gas saturation and

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Fig. 1. Flow cross-section of the assumed pore network and phase distribution model to estimate the specific interfacial area.
capillary pressure reduces the interfacial area, as always the smallest pores are preferably filled up by the water phase.

For the specific interfacial area between the water and the solid phase we find for the assumed pore network model, see also Bear (1972), that

$$a_{ws} = 6(1 - \phi)/d_k. \tag{25}$$

2.5.3. Distribution coefficients at thermodynamic equilibrium

To estimate the fictitious gas phase concentration $[\rho_g X_g]_{eq}$ at thermodynamic equilibrium between the gas and water phase, we evaluate the VCHC fugacity in the gas phase with Dalton’s law (ideal gas) and in the water phase with Henry’s law (ideal dilution). At thermodynamic equilibrium (equal chemical potential in both phases) we get:

$$H_k := \frac{[\rho_g X_g]_{eq}}{\rho_w X_w^K} = \frac{h^k}{M_w RT \sum^n_{i=1} \frac{x_i^w}{M_i}}, \tag{26}$$

where $R$ is the ideal gas constant, $h^k$ is the Henry coefficient, which in turn results from integration of the Clausius–Clapeyron differential equation (Heron et al., 1998).

To estimate the fictitious water phase concentration $[\rho_w X_w^K]_{eq}$ at thermodynamic equilibrium between the water and solid phase, we use the linear Freundlich isotherm:

$$K_d^K := \frac{X_S^K}{[\rho_w X_w^K]_{eq}}. \tag{27}$$

Zhang et al. (1990a,b) indicate that in a dilute aqueous solution a linear adsorption isotherm requires that the concentration of a solute in the interfacial region is proportional to the concentration of the solute in the bulk phase.

2.5.4. Mass transfer rate coefficients

If we use Eq. (26), to replace the fictitious concentrations $[\rho_\alpha X_\alpha^K]_{ph}$ and $[\rho_\alpha X_\alpha^K]_{eq}$ in Eq. (19), then we get for the gas–water mass transfer rate coefficient the result

$$\frac{1}{\gamma^K_{gw}} = \frac{1}{a_{gw}} \left( \frac{1}{\gamma^K_{gw}} + H_k \right). \tag{28}$$

Roberts et al. (1985) and Szatkowski et al. (1994) used the same approach to calculate the gas–water mass transfer rate coefficient of VCHC in porous media.

If we combine in the same way Eqs. (27) and (19), then we get for the water–solid mass transfer rate coefficient the result

$$\frac{1}{\gamma^K_{ws}} = \frac{1}{a_{ws}} \left( \frac{1}{\gamma^K_{ws}} + \frac{1}{\gamma^K_{s} K_d^K} \right). \tag{29}$$

We adopt the two-film model also for the water–solid mass transfer, as we deal later with solid quartz grains as sorbent in which no intra-aggregate diffusion of VCHC occurs.
Otherwise we would have to use an aggregate diffusion model (Goltz and Roberts, 1986; Gierke et al., 1992; Ng and Mei, 1996, 1999).

2.6. Thermodynamic equilibrium indicators

After describing mathematically the contaminant transport and interfacial transfer processes of the \( n \)-component and three-phase system considered, the balance equations are transformed into dimensionless form, assuming a simplified model problem. From this, first insights can be obtained about the significance of single model parameters for the interfacial mass transfer. In particular, expressions indicating thermodynamic equilibrium are defined for the kinetic gas–water and water–solid mass transfer. Those are used to explain the VCHC specific behavior shown in the laboratory experiment of Section 4.

We restrict our dimensionless analysis to a 1d domain of length \( L \) and consider a one-component and three-phase system. All secondary physical and chemical variables describing gas, water and solid phase are uniform in time and space. We insert Eq. (11) into Eq. (1) and get

\[
\phi S_g \frac{\partial C_g}{\partial t} + \phi S_w \frac{\partial C_w}{\partial t} + (1 - \phi) \rho_s \frac{\partial X_s}{\partial t} + \phi S_g \left( v_g \frac{\partial C_g}{\partial x} - D_{hyd}^g \frac{\partial^2 C_g}{\partial x^2} \right) = 0, \tag{30}
\]

where \( C_a = \rho_a X_a \) is the volume-specific mass (concentration) of an arbitrary VCHC in phase \( \alpha \). \( D_{hyd}^g \) is the coefficient of hydrodynamic dispersion in the gas phase. With regard to Eqs. (17), (26) and (27), Eqs. (2) and (3) are equivalent to

\[
\phi S_w \frac{\partial C_w}{\partial t} = \gamma_{gw}(C_g - C_w H) - \gamma_{ws}(C_w - X_s/K_d), \tag{31}
\]

and

\[
(1 - \phi) \rho_s \frac{\partial X_s}{\partial t} = \gamma_{ws}(C_w - X_s/K_d). \tag{32}
\]

As initial condition, at \( t = 0 \), we choose on \( 0 \leq x \leq L \)

\[
C_w(0, x) = C_g(0, x)/H \tag{33}
\]

and

\[
X_s(0, x) = C_w(0, x)K_d. \tag{34}
\]

The following dimensionless variables are introduced:

\[
C_g^* := C_g / C_g(0, x), \quad C_w^* := C_w / C_w(0, x), \quad C_s^* := X_s / X_s(0, x), \tag{35}
\]

\[
t^* := t v_g / L, \tag{36}
\]

\[
x^* := x / L, \tag{37}
\]

\[
Pe := v_g L / D_{hyd}^g, \tag{38}
\]

\[
St_{gw} := \gamma_{gw} L / v_g. \tag{39}
\]
and
\[
St_{ws} := \gamma_{ws} L / \nu_g.
\] (40)

Here \( Pe \) is the Peclet number, \( St \) is the so-called Stanton or Damköhler number. Now, Eqs. (30)–(32) are transformed into
\[
\frac{\partial C_g^*}{\partial t^*} + \frac{\phi S_w}{H} \frac{\partial C_w^*}{\partial t^*} + \frac{(1 - \phi) \rho_s K_d}{H} + \frac{\partial C_s^*}{\partial t^*} + \phi S_g \left( \frac{\partial C_g^*}{\partial x^*} - \frac{1}{Pe} \frac{\partial^2 C_g^*}{\partial x^*^2} \right) = 0,
\] (41)
\[
\frac{\partial C_w^*}{\partial t^*} = \frac{HS_{gw}}{\phi S_w} (C_g^* - C_w^*) - \frac{St_{ws}}{\phi S_w} (C_w^* - C_s^*)
\] (42)
and
\[
\frac{\partial C_s^*}{\partial t^*} = \frac{St_{ws}}{(1 - \phi) \rho_s K_d} (C_w^* - C_s^*),
\] (43)

with the initial condition
\[
C_g^*(0, x^*) = C_w^*(0, x^*) = C_s^*(0, x^*) = 1.
\] (44)

From the Equation System (41)–(44) we expect for arbitrary boundary conditions rather small values \(|C_g^*(t^*, x^*) - C_w^*(t^*, x^*)|\) for the case of \( HSt_{gw}/(\phi S_w) \gg 1 \) and \( HSt_{gw} \gg St_{ws} \),
\] (45)
as well as rather small values \(|C_w^*(t^*, x^*) - C_s^*(t^*, x^*)|\) for the case of \( St_{ws}/((1 - \phi) \rho_s K_d) \gg 1 \),
\] (46)
for \( t^* \in [0, \infty) \) and \( x^* \in [0, 1] \). The more strongly these conditions are fulfilled, the more closely a thermodynamic gas–water equilibrium or water–solid equilibrium can be reached for a fixed \( t^* \in [0, \infty) \) and \( x^* \in [0, 1] \).

### 3. Numerical solution

There are several possibilities for discretizing the system of partial and ordinary differential Eqs. (1)–(4) on a 2d domain. The method of lines approach (MOL) discretizes in space and treats the resulting discrete system of ordinary differential equations by classical ODE procedures (Fletcher, 1988; Lichtner et al., 1996). Further methods are suggested by Bornemann (1992), Wagner (1998), Lang (1999) or Eriksson and Johnson (1995).

For our numerical simulations, we use the software framework UG (Bastian et al., 1997), which allows for the parallel adaptive solution of a large variety of partial differential equations in two and three space dimensions. For advection–dispersion–interfacial transfer systems, it provides the MOL approach in an adaptive setting. The
Spatial discretization is done by a finite volume method (see Section 3.1) which is embedded inside an implicit Euler scheme (see Section 3.2). The resulting numerical solution of the model problem (1)–(4) is tested analytically and semi-analytically by Hoeg (2001) on a one-dimensional cartesian domain.

### 3.1. Spatial discretization

For discretization in space, we use a vertex-centered finite volume scheme, also called box method, which we want to sketch briefly. We choose on a closed domain \( \Omega \subset \mathbb{R}^N \) \((N=2)\) a grid \( \mathcal{T} \) consisting of vertices \( v_j, j \in \mathcal{L} \), which are corners of elements \( e_v, v \in \mathcal{V} \) (2d: triangles, quadrangles). Here \( \mathcal{L} \) and \( \mathcal{V} \) are suitable index sets. By connecting the barycenters of the elements \( e_v \) around the vertices \( v_j \), one obtains a dual grid \( \mathcal{B} \) consisting of control volumes \( B_j \subset \Omega \), also called boxes.

Then, a discrete system is obtained by integrating Eqs. (1)–(4) over the boxes \( B_j \) and replacing the unknowns \( p_g^2 \) and \( X_\alpha^k \) by approximations that are piecewise linear, bilinear or multi-linear depending on the geometry of the elements. This approach is well known and can be found at many places, see, e.g. Bey (1998) and Bastian (1999) for a detailed description. Note, that primary variable \( p_g^2 \) results from applying the chain rule to Eq. (4) (total mass balance) after inserting Eq. (5) (ideal gas law) and Eq. (7) (Darcy’s law). The diffusion tensors and convection vector fields in Eq. (1) are assumed to be constant on elements and are evaluated by midpoint rules. For the convective terms, full up-winding is used to avoid spurious oscillations.

### 3.2. Time stepping scheme

Let \( y(t_k)=[p_g^2(t_k), X_\alpha^k(t_k)] \) be an approximation to the solution of Eqs. (1)–(4) discretized in space from the previous section. We then use the following time-stepping scheme to obtain a discrete approximation \( y(t_{k+1})=[p_g^2(t_{k+1}), X_\alpha^k(t_{k+1})] \) at time \( t_{k+1} = t_k + \Delta t \):

(i) The space-discretized form of the scalar elliptic Eq. (4) is solved by a standard multigrid iteration. From here we get the spatial distribution of \( p_g^2 \).

(ii) We replace the time derivatives in the space-discretized form of Eqs. (1)–(3) with backward differences (implicit Euler method). Due to the interfacial mass transfer term \( m_{ij}^k \), the discrete equations will still be non-linear in general. Applying Newton’s method, we end up with a linear system that we solve by a standard multigrid iteration using a point-block Gauss-Seidel smoother. Here the blocks correspond to all values \( X_\alpha^k \) at one vertex \( v_j \).

(iii) For step size control we halve time step \( \Delta t \) if the mean convergence rate of the Newton method is slower than a given threshold \( \rho_{\text{mean}} \). The time step \( \Delta t \) is doubled, if the convergence rate of the first Newton iteration is faster than a given threshold \( \rho_{\text{first}} \). Furthermore, the time step \( \Delta t \) is confined by a given upper and lower boundary.

(iv) We use an hierarchical error estimator measuring the square of the differences between the values of \( X_\alpha^k(t_{k+1}) \) and \( p_g^2(t_{k+1}) \) on subsequent levels. This local quantity measures the interpolation error and can be used as an indicator for
refinement and coarsening. An upper limit for the number of grid levels avoids excessive refinement along sharp fronts.

The linear system, which has to be solved in step (i) has a very special structure that can be used to improve storage requirements and computational speed, see Neuß (1999).

4. Results

After having described the mathematical modeling and numerical solution scheme, we apply the numerical model to a two-dimensional test problem. This happens on the basis of a laboratory experiment of Fischer et al. (1996), in which rate limited gas–water mass transfer of several VCHC—induced by a stationary gas flow—has been investigated in a water unsaturated quartz sand packing.

4.1. SVE experiment

A tank (Fig. 2) of dimensions $72 \times 66 \times 5$ cm was homogeneously packed with quartz sand of grain sizes in the range of 0.08–1.2 mm. A relative small (experiment V1), mean (experiments V2 and V4) and large (experiment V3) volume of Nanopure water was added. In order to achieve hydrodynamic equilibrium, each experiment was started 3 months after the infiltration of the water.

In the following we consider experiment V2. The spatial distribution of the water saturation $S_w$ was calculated by Fischer et al. (1996) from the volume of infiltrated water using the software MUNETOS (Zuhrmühl, 1994) and using the parameters describing the water retention curve determined for the wetting process. In doing so, 0.54 and 0.08 were determined as the largest and smallest water saturations (Fig. 3).

![Fig. 2. Experimental setup of Fischer et al. (1996).](image-url)
In order to establish a homogeneous initial distribution of the VCHC, a small volume of a liquid mixture containing 1,1,1-trichloroethane (1,1,1-TCA), 1,1,2-trichloroethane (1,1,2-TCA), trichloroethylene (TCE) and perchloroethylene (PCE) was released into one of the wells. Gas samples were subsequently taken to monitor the spreading of the compounds. After about 2 weeks the VCHC were found to be evenly distributed over the tank, and the venting experiment was started. A liquid organic phase (NAPL) was not present in the water unsaturated quartz sand packing. Values of the water–solid distribution coefficients $K_{d}$ determined in batch experiments for the four VCHC were not significantly different from zero. A stationary gas flow was induced by means of a membrane pump. Pressure transducers were used to monitor the applied pressure difference of 14 Pa between the injection and extraction well. The supplied air was first dried using silica gel, then purified by activated carbon cartridges, and subsequently humidified to a relative humidity of 98% to avoid water losses from the tank. During the venting (22 h) 12 gas phase samples were taken for gas chromatographic analysis of VCHC at each sampling port (SP) 13, 23, 33 and 43. Concerning the precision of analytical procedure, coefficients of variation were generally below 2.5%. For further description Table 1 gives a summary of parameter values determined by Fischer et al. (1996).

4.2. Numerical simulations

Computations are done on a rectangular unstructured multigrid (Fig. 13) consisting of seven to eight grid levels using the time stepping scheme described in Section 3.2.
Concerning the primary variables $X_g, j \in \{1,1,1\text{-TCA, 1,1,2\text{-TCA, TCE, PCE}\}$, we choose the Neumann condition $\nabla X_g \bullet n = 0$ at the two boundaries parallel to the flow ($x=0 \ldots 0.72 \text{ m}, y=0 \text{ m or } y=0.66 \text{ m}$) and at the outflow boundary ($x=0.72 \text{ m}, y=0 \ldots 0.66 \text{ m}$). Furthermore, the Cauchy condition

$$\phi S_g \rho_g X_g^k v_g \bullet n - \phi S_g F_g^k \bullet n = 0$$

is valid at the inflow boundary ($x=0 \text{ m}, y=0 \ldots 0.66 \text{ m}$). For the primary variables $X_w^k$ and $X_s^k, k \in \{1,1,1\text{-TCA, 1,1,2\text{-TCA, TCE, PCE}\}$, we choose the Neumann condition $\nabla X_w^k \bullet n = \nabla X_s^k \bullet n = 0$ at all boundaries. For the primary variable $p_g^2$ we select the Neumann condition $\nabla p_g^2 \bullet n = 0$ at the boundaries parallel to the flow ($x=0 \ldots 0.72 \text{ m}, y=0 \text{ m or } y=0.66 \text{ m}$). At the inflow and outflow boundary the Dirichlet condition $p_g^2 = p_{atm}$ and $p_g^2 = (p_{atm} - 14)^2$ is selected.

As initial condition, at $t=0$, we choose for the primary variables $X^k$ a distribution at thermodynamic equilibrium, see Eqs. (33) and (34), on the whole domain.

4.3. Gas phase and water phase in thermodynamic non-equilibrium, sorption processes neglected

In order to fit the measured VCHC gas phase concentrations at SP 13, 23, 33 and 43, we scaled the diffusion lengths $l_g$ and $l_w$, the specific interfacial area $a_{gw}$ and the resulting specific mass transfer rate coefficients $\gamma_{gw}^k$ by varying the grain diameter $d_k$, which may not be inside the measured range for all simulations, as we tried to find a characteristic length scale of an idealized pore network and phase distribution model (see Section 2.5.2). Besides the grain diameter $d_k$ and the measured parameter values in Table 1, basic physical and chemical properties of the gas phase, water phase and

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length of the domain [m]</td>
<td>0.72</td>
</tr>
<tr>
<td>Height of the domain [m]</td>
<td>0.66</td>
</tr>
<tr>
<td>Temperature $T$ [K]</td>
<td>295.15 ± 1.0</td>
</tr>
<tr>
<td>Porosity of sand packing $\phi$ [-]</td>
<td>0.36</td>
</tr>
<tr>
<td>Bulk density $\rho_s$ [kg/m$^3$]</td>
<td>1680</td>
</tr>
<tr>
<td>Grain diameter $d_k$ [m]</td>
<td>$8.0 \times 10^{-5} \ldots 1.2 \times 10^{-3}$</td>
</tr>
<tr>
<td>Residual water saturation $S_{wr}$ [-]</td>
<td>0.16</td>
</tr>
<tr>
<td>Van Genuchten parameter $n$ [-]</td>
<td>3.1</td>
</tr>
<tr>
<td>Van Genuchten parameter $m$ [-]</td>
<td>$1 - 1/n$</td>
</tr>
<tr>
<td>Gas saturation at which gas flow emerges/extends $S_{ge}$ [-]</td>
<td>0.42</td>
</tr>
<tr>
<td>Intrinsic permeability $K$ [m$^2$]</td>
<td>$6.0 \times 10^{-11}$</td>
</tr>
<tr>
<td>Applied pressure difference [Pa]</td>
<td>14</td>
</tr>
<tr>
<td>Duration of venting [h]</td>
<td>22</td>
</tr>
<tr>
<td>1,1,1-TCA initial gas phase concentration [mol/m$^3$]</td>
<td>$1.9 \times 10^{-3}$</td>
</tr>
<tr>
<td>1,1,2-TCA initial gas phase concentration [mol/m$^3$]</td>
<td>$7.1 \times 10^{-4}$</td>
</tr>
<tr>
<td>TCE initial gas phase concentration [mol/m$^3$]</td>
<td>$1.3 \times 10^{-3}$</td>
</tr>
<tr>
<td>PCE initial gas phase concentration [mol/m$^3$]</td>
<td>$6.9 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
VCHC were obtained from Reid et al. (1987) and Lide (1997). Temporal and spatial variations of secondary variables are comparatively small (1–5%) due to isothermal conditions as well as comparatively low contaminant concentrations and pressure gradients (Table 2). The mass flux of mechanical dispersion is supposed to be in range of the molecular diffusive mass flux for the occurring Peclet numbers at the pore scale ($Pe<10$) (Domenico and Schwartz, 1990) and is neglected for the first simulations ($\alpha_L = \alpha_T = 0$ m).

Selecting a grain diameter of $d_k = 5.0 \times 10^{-2}$ m yields a diffusion length near the interfacial contact area $l_w$ of $2.5 \times 10^{-2}$ m (Eq. (20)) and a specific interfacial area $a_{gw}$ (Eq. (24)) between 26.0 and 37.0 m$^{-1}$ (see Fig. 4c). The selected size of the grain diameter $d_k$ is outside the measured range, see Table 1. Gas–water mass transfer rate coefficients $\gamma_{gw}^K$ of VCHC (Eq. (28)) are between $1.0 \times 10^{-6}$ and $4.0 \times 10^{-5}$ s$^{-1}$ (see Fig. 4b). 1,1,2-TCA has the largest gas–water mass transfer rate coefficients as a result of its relative low volatility, i.e. gas–water distribution coefficient, and moderate molecular diffusivity in water (Table 2). Concerning gas–water mass transfer, all VCHC are distinctly in thermodynamic non-equilibrium with $H_{St_{gw}/(\phi S_w)}$ values between $3.0 \times 10^{-2}$ and 0.4 (see Fig. 4a).

Except for 1,1,2-TCA, time series of experimental gas phase concentrations are matched comparatively well at all sampling ports (Fig. 5). However, in contrast to the simulated time series, experimental ones decline in sequence of the gas–water distribution coefficients ($H^{1,1,2-TCA} < H^{TCE} < H^{PCE} < H^{1,1,1-TCA}$) for early times of the experiment. Since a NAPL phase was absent in the water unsaturated quartz sand packing and given the model assumptions in Section 2 such a strong influence of VCHC vapor pressures can be explained only by much larger values of the gas–water equilibrium indicator $H_{St_{gw}/(\phi S_w)}$ (Eq. (45)). Thus, for the next simulation we moved the system closer to gas–water thermodynamic equilibrium conditions, i.e. we enlarged the gas–water Stanton number $St_{gw}$ (Eq. (39)) through a reduction of the grain diameter $d_k$.

### 4.4. Gas phase and water phase in thermodynamic equilibrium, sorption processes neglected

Shifting of the grain diameter to $d_k = 5.0 \times 10^{-4}$ m yields a diffusion length near the interfacial contact area $l_w$ of $2.5 \times 10^{-4}$ m (Eq. (20)) and a specific interfacial area $a_{gw}$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>1,1,1-TCA</th>
<th>1,1,2-TCA</th>
<th>TCE</th>
<th>PCE</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H^*$ [-]</td>
<td>0.63</td>
<td>0.03</td>
<td>0.36</td>
<td>0.60</td>
<td>Anwar et al., 2000</td>
</tr>
<tr>
<td>$D_g^K$ [m$^2$/s]</td>
<td>$7.94 \times 10^{-6}$</td>
<td>$7.94 \times 10^{-6}$</td>
<td>$8.10 \times 10^{-6}$</td>
<td>$7.38 \times 10^{-6}$</td>
<td>Armstrong et al., 1994</td>
</tr>
<tr>
<td>$D_w^K$ [m$^2$/s]</td>
<td>$8.56 \times 10^{-10}$</td>
<td>$8.56 \times 10^{-10}$</td>
<td>$8.91 \times 10^{-10}$</td>
<td>$8.02 \times 10^{-10}$</td>
<td>Ball and Roberts, 1991</td>
</tr>
</tbody>
</table>

References: Anwar et al., 2000, Eq. (26); Armstrong et al., 1994, Eq. (14); Ball and Roberts, 1991, Hayduk and Laudie (1974). Basic physical and chemical properties of the gas phase, water phase and VCHC were obtained from Reid et al. (1987) and Lide (1997).
(Eq. (24)) between 2600 and 3700 m\(^{-1}\) (see Fig. 6c). The selected size of the grain diameter \(d_k\) is now inside the measured range, see Table 1. Gas–water mass transfer rate coefficients \(\gamma_{gw}\) of VCHC (Eq. (28)) are between 1.0 \(\times\) 10\(^{-2}\) and 4.0 \(\times\) 10\(^{-1}\) s\(^{-1}\).
Concerning gas–water mass transfer, all VCHC are distinctly in thermodynamic equilibrium with $H_j S_{gw}/S$ values between 300 and $4.0 \times 10^3$ (see Fig. 6a).

Fig. 5. Comparison between simulation and experiment for the gas–water system using an effective grain diameter of $d_k = 5.0 \times 10^{-2}$ m: (a) SP 13, (b) SP 23, (c) SP 33, (d) SP 43.

Both simulated and measured time series decline in sequence of the VCHC gas–water distribution coefficients for early times of the experiment (Fig. 7). However, PCE leaves this vapor pressure induced sequence with comparative high gas phase concentrations during later stages, though having the lowest molecular diffusivity (Table 2). Except for 1,1,2-TCA, time series of experimental gas phase concentrations are matched comparatively bad at later stages at all sampling ports. The measured data are increasingly underestimated with progressing time. The available mass of 1,1,1-TCA, TCE and PCE computed for the water phase is insufficient to keep the relative high experimental gas phase concentrations during the final stage of the experiment. Since a liquid organic phase was absent in the tank, we included the solid phase as an additional contaminant mass reservoir for the following simulations.
Fig. 6. Parameter values versus tank height $h$ [m] at $L = 0.41$ m and $t = 0$ s for the gas–water system using a grain diameter of $d_k = 5.0 \times 10^{-4}$ m: (a) gas–water equilibrium indicator $H_{gw}^{*}St_{gw}^{*}/(\phi \cdot S_w)$, (b) gas–water mass transfer rate coefficient $\gamma_{gw}^{*}$ [1/s], (c) gas–water specific interfacial area $a_{gw}$ [1/m].
4.5. Gas phase and water phase in thermodynamic equilibrium, water phase and solid phase in weak thermodynamic non-equilibrium

In order to consider the tendency of the contaminants to adsorb on the quartz surface, the water–solid distribution coefficients $K_d^k$ (Eq. (27)) are estimated simply on the basis of octanol–water distribution coefficients $K_{ow}^k$:

$$K_d^k = c \ K_{ow}^k,$$  \hspace{1cm} (48)

Table 3
Water–solid distribution coefficients $K_d^k$ [m³/kg] using Eq. (48) with $c = 9.0 \times 10^{-8}$ [m³/kg]

<table>
<thead>
<tr>
<th>CKW</th>
<th>$K_{ow}^k$</th>
<th>$K_d^k$ [m³/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1,1-TCA</td>
<td>302.00</td>
<td>$2.72 \times 10^{-5}$</td>
</tr>
<tr>
<td>1,1,2-TCA</td>
<td>112.20</td>
<td>$1.01 \times 10^{-5}$</td>
</tr>
<tr>
<td>TCE</td>
<td>263.03</td>
<td>$2.37 \times 10^{-5}$</td>
</tr>
<tr>
<td>PCE</td>
<td>758.58</td>
<td>$6.83 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
Fig. 8. Parameter values versus tank height $h$ [m] at $L = 0.41$ m and $t = 0$ s for the gas–water–sand system using a grain diameter of $d_k = 5.0 \times 10^{-4}$ m and $K_d$ values of Table 3: (a) gas–water equilibrium indicator $H^k St_{gw}^k/(\phi S_w)$, (b) water–solid equilibrium indicator $St_{ws}^k/((1-\phi) \rho_g K_d)$, (c) gas–water mass transfer rate coefficient $\gamma_{gw}^k [1/s]$, (d) water–solid mass transfer rate coefficient $\gamma_{ws}^k [1/s]$, (e) gas–water specific interfacial area $a_{gw} [1/m]$, (f) water–solid specific interfacial area $a_{ws} [1/m]$. 
where $c$ is a fitting parameter, set to $9.0 \times 10^{-8}$ m$^3$/kg for the simulation. The resulting water–solid distribution coefficients $K_d^j$ are low (Table 3). The solid phase diffusion coefficients of the contaminants were set equal to the binary aqueous phase diffusion coefficients, i.e. $D_{j,s} = D_{j,w}$ (Table 2).

Retaining the grain diameter at $d_k = 5.0 \times 10^{-4}$ m yields diffusion lengths $l_w$ and $l_s$ of $2.5 \times 10^{-4}$ m (Eq. (20)). The specific interfacial area $a_{ws}$ (Eq. (25)) is $7680$ m$^{-1}$ (see Fig. 8f). Water–solid mass transfer rate coefficients $\gamma_{ws}^K$ of VCHC (Eq. (29)) are between $2.0 \times 10^{-7}$ m and $2.0 \times 10^{-6}$ s$^{-1}$ (see Fig. 8d). PCE has the largest water–solid mass transfer rate coefficients as a result of its comparatively high sorptivity (Table 3), though having the lowest molecular diffusivity (Table 2). Concerning water–solid mass transfer, all VCHC are slightly in thermodynamic non-equilibrium with $St_{ws}^K / \left( (1 - \phi) \rho_s K_d^j \right)$ values between $4.0 \times 10^{-2}$ and 2.0 (see Fig. 8b).

Time series of experimental gas phase concentrations are matched well at sampling ports 23 and 33 (Fig. 9). Gas phase concentrations are overrated at SP 13. The volatility

![Fig. 9. Comparison between simulation and experiment for the gas – water – sand system using an effective grain diameter of $d_k = 5.0 \times 10^{-4}$ m and $K_d^j$ values of Table 3: (a) SP 13, (b) SP 23, (c) SP 33, (d) SP 43.](image-url)
Fig. 10. Parameter values versus tank height $h$ [m] at $L = 0.41$ m and $t = 0$ s for the gas–water–sand system using a grain diameter of $d_k = 5.0 \times 10^{-4}$ m and a unique $K_a$ value of $3.0 \times 10^{-5}$ m$^3$/kg: (a) gas–water equilibrium indicator $H^X \cdot St_{gw}^X / (\phi \cdot S_{gw})$, (b) water–solid equilibrium indicator $St_{ws}^X / ((1 - \phi) \cdot \rho \cdot K_{d}^X)$, (c) gas–water mass transfer rate coefficient $\gamma_{gw}^X [1/s]$, (d) water–solid mass transfer rate coefficient $\gamma_{ws}^X [1/s]$, (e) gas–water specific interfacial area $a_{gw} [1/m]$, (f) water–solid specific interfacial area $a_{ws} [1/m]$. 
of the contaminants \( (H_{1,2-TCA}^1 < H_{TCE}^1 < H_{PCE}^1 < H_{1,1,1-TCA}^1) \) is reflected in early sections of both measured and simulated time series, the sorptivity of the contaminants \( (K_{dTCA}^{1,4-TCA} < K_{dTCE}^1 < K_{dTCA}^{1,1,1-TCA} < K_{dPCE}^1) \) is reflected in later sections of both measured and simulated times series. That is visible especially for PCE with gas phase concentrations declining relatively fast during the beginning and relatively slow during the end of the experiment, as a result of its high volatility and sorptivity.

The described behavior cannot be explained only by the VCHC specific diffusivities, as shown by a simulation using a unique \( K_d^i \) value of \( 3.0 \times 10^{-5} \) m\(^3\)/kg (Figs. 10 and 11). In this case the tailing of the contaminants is not reflected correctly. This shows that VCHC specific \( K_d^i \) values should be considered, as already indicated by the scale of \( St_{ws}^i/(1 - \phi)\rho_s K_d^i \), which suggests no strong thermodynamic non-equilibrium between the water phase and solid phase.

![Comparison between simulation and experiment for the gas–water–sand system using a grain diameter of \( d_k = 5.0 \times 10^{-4} \) m and a unique \( K_d^i \) value of \( 3.0 \times 10^{-5} \) m\(^3\)/kg: (a) SP 13, (b) SP 23, (c) SP 33, (d) SP 43.](image-url)
Furthermore, inclusion of a mechanical dispersive flux \( (a_L = 0.072 \, \text{m}, \ a_T = 0.0072 \, \text{m}) \) in range of the molecular diffusive flux does not strongly affect the simulated time series (Fig. 12).

5. Discussion

5.1. Sorption of less or non-polar VCHC on quartz sand

As shown in Sections 4.3 and 4.4, the time series of the experimental gas phase concentrations cannot be explained only by the diffusivity and volatility of the VCHC—there must be a further process, and its significance grows according to 1,1,2-TCA < TCE < 1,1,1-TCA < PCE.

Before the venting experiment was started, the water phase (Nanopure water) was in contact with the quartz sand packing for more than 3 months. Such polar mineral
surfaces, consisting of atoms poor in electrons (Si) and ligands rich in electrons (O), expose several hydroxyl groups that tend to build strong dipole–dipole interactions (hydrogen bonds) with molecules near the mineral surface. The charge and polarity render the mineral surfaces hydrophilic and contribute to a structuring of the water adjacent to the mineral surface. This ordering effect extends over several successive molecule layers at the nanometer scale. Because it is energetically unfavorable for non-polar organic contaminants to displace water from hydrophilic mineral surfaces, organic compound partitioning into structured water is the commonly accepted mechanism for adsorption of hydrophobic organic compounds on minerals (Zhang et al., 1990a,b; Schwarzenbach et al., 1993; Xing et al., 1996). At relative humidities between 30% and 90% the same kind of process has been postulated for the adsorption of organic vapors on quartz sand (Rhue et al., 1989; Goss, 1992; Goss and Eisenreich, 1996). According to Schwarzenbach et al. (1993) a description of the sorptivity of less or non-polar organic molecules on polar mineral surfaces in aqueous solution should include the advantage that these molecules gain when they escape from the disordered water phase into rather ordered water molecule layers near the mineral surface. It is expected that the free energy of sorption of less or non-polar organic molecules is inversely related to the free energy of these molecules in aqueous solution. A measure for the latter is the so-called aqueous activity coefficient $\gamma^*_W$, being a bulk parameter to describe non-ideal effects of the aqueous dissolution process. For less or non-polar VCHC it can be shown that the aqueous activity coefficient is directly proportional to the octanol–water distribution coefficient $K_{ow}$ (see Appendix B).

Several restrictions for the so-called vicinal water hypothesis have been observed. Schlautman and Morgan (1994) report that at neutral to high pH the binding of cations like Na$^+$ at the silica surface become increasingly important in determining adsorption rates for e.g. perylene. Furthermore, the partitioning of organic compounds into structured water can be superimposed by processes that involve micropores in the surface of a porous silica (Schwarzenbach and Westall, 1981; Farrell et al., 2002). Fischer (2001) analyzed the surface of the quartz grains using a grid electron microscope and found only inlets but no deeper pores or fissures.

Nevertheless, detailed experimental evidence for the postulated sorption process cannot be provided and even other sorption mechanisms have to be discussed. Impurities of organic matter, e.g. in the form of organic coatings around the quartz grains, could produce sorption effects that depend on the hydrophobicity of the organic compounds, similar to the vicinal water hypothesis. This has been shown for sorbents with adequate amounts of organic carbon (e.g. $f_{oc}>0.001$) (Chiou et al., 1979; Schwarzenbach and Westall, 1981; Curtis et al., 1986) and is believed to occur via a dual partition/holefilling mechanism (Xing et al., 1996). Fischer (2001) reported a very low organic carbon content for the investigated quartz sand packing. It cannot be ruled out absolutely that minor impurities contribute or even lead to a VCHC specific sorption behavior as described in Section 4.5.

Sorption processes have been neglected in an earlier numerical investigation on this experiment, since Fischer et al. (1996) found values of water–solid distribution coefficients $K_d$ (determined in batch experiments) not significantly different from zero. The suggested water–solid distribution coefficients $K_d$ of this numerical investigation,
being between $1.10 \times 10^{-5}$ and $6.83 \times 10^{-5}$ m$^3$/kg (Table 3), can be considered Likewise as very low.

5.2. Role of geometry

Schlautman and Morgan (1994) remark that—when examining data over a wide range of solute hydrophobicity—a clear correlation exists between the partitioning of organic compounds into structured water and the aqueous activity coefficient, if adsorption constants are normalized by the surface area of the minerals. The presented modeling approach proceeds in a similar way by trying to structure the mathematical model into VCHC specific and VCHC non-specific parameters, i.e. parameters that are related to the molecular structure of the VCHC (like the volatility, diffusivity or aqueous activity) and parameters that are related to the physical surrounding of chemical compounds (e.g. diffusion length, interfacial area or phase saturation). Given the model assumptions described in Section 2 the suggested thermodynamic equilibrium indicators help to identify those physical parameters that may limit the interfacial mass transfer. Furthermore, they indicate if the VCHC specific mass flux is rather influenced by parameters that describe kinetic processes, like the diffusivity of the organic compound, than by parameters that describe thermodynamic states, like the volatility and sorptivity of the organic compound. In our case the range of the gas–water equilibrium indicator $H^o S_{gw}/(\phi S_w)$, being between 300 and $4.0 \times 10^3$ (Fig. 8a), corresponds to the strongly developed thermodynamic effects in earlier sections of the measured VCHC time series (Fig. 9), i.e. the gas phase concentrations of the organic compounds decline in sequence of their gas–water distribution coefficients $H^o$, which results from the compound specific velocity of the evaporation front (Fig. 13). Whereas the range of the water–solid equilibrium indicator $St_{ws}/((1/\phi)\rho_s K_d)$, being between $4.0 \times 10^{-2}$ and 2.0 (Fig. 8b), corresponds to the simultaneously occurring thermodynamic and kinetic effects in later sections of the measured VCHC time series (Fig. 9), i.e. the gas phase concentrations of the organic compounds decline in sequence of their water–solid distribution coefficients $K_d$, but showing a less gradient due to some diffusional resistance.

The assumed pore network model and phase distribution model (Fig. 1) may be idealized, but it can be scaled by one single parameter, namely the grain diameter $d_k$, which simplifies essentially the scaling and calibration of our mathematical model and guards against any chemical compound specific parameter fitting. On the basis of uniform spherical aggregates Ng and Mei (1999) explain and predict several complex phenomena from the basic principles that are related to the multicomponent dynamics of SVE systems in unsaturated soils with mass exchange kinetics due to free and trapped phases of residual NAPL. The geometric idealization enables a complete coupling between the microscale and macroscale transports and between the individual less or more volatile components. Furthermore, Ng and Mei (1999) stress that the amount of calibration will be limited and does not increase with the number of components, as it does for models in which calibration must be carried out separately for each component.

We think that an idealization of the pore network model and phase distribution may be even helpful for the modeling of real world applications where strongly developed and
measureable spatial heterogeneities may occur, as long as the numerical model is able to spatially discretize those heterogeneities in uniform control volumes. This is feasible when adaptive techniques together with an adequate fast numerical solution scheme, as described in Section 3, are used.

Fig. 13. Water phase mass fraction $X_{w}^{j}$ of 1,1,2-TCA and PCE on adaptive grid at time step no. 3 (a and b), no. 10 (c and d) and no. 20 (e and f). Simulation for the gas–water–sand system using an effective grain diameter of $d_k = 5.0 \times 10^{-4}$ m and $K^k$ values of Table 3. See also Figs. 8 and 9.
6. Summary and conclusions

We have described an isothermal n-component and three-phase model that accounts—beyond gas flow and contaminant transport—in particular for interfacial mass transfer kinetics (gas–liquid, liquid–solid) of VCHC. The model has several features designed to improve the assessment of thermodynamic and kinetic effects that may occur in SVE systems:

1. Assuming an idealized pore network and phase distribution, the model is structured into VCHC specific and non-specific parameters, which enables us to separate physicochemical properties of single VCHC from geometrical constraints of the porous medium.

2. The model is scaled by one single parameter, namely the grain diameter $d_k$ that represents the characteristic length scale. This simplifies the calibration of the model and guards against a VCHC specific parameter fitting. In addition, dimensionless expressions were derived indicating thermodynamic equilibrium or non-equilibrium conditions with respect to the gas–liquid and liquid–solid mass transfer. These indicators help to identify those physical parameters that limit interfacial mass transfer.

3. A numerical scheme is developed that solves implicitly two or three dimensional flow, transport and interfacial mass transfer equations of an isothermal n-component and three-phase system, which allows to apply the prior suggestions to any real world application that fulfills the model assumptions.

The model was used to re-analyse data of a laboratory experiment of Fischer et al. (1996). The analysis suggests that long-term fading of VCHC in the gas phase in that experiment was controlled not only by their volatility and diffusivity in the water phase, but also by a desorption process whose significance grows with the octanol–water distribution coefficient, which is shown to be proportional to aqueous activity in the case of the investigated less or non-polar organic compounds.

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Appendix A. Notation

*Latin symbols*

$a_{\alpha\beta}$ volume-specific interfacial area between phase $\alpha$ and $\beta$, (1/m)

$B_k$ control volume
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mathcal{B}$</td>
<td>dual grid</td>
</tr>
<tr>
<td>$c$</td>
<td>fitting parameter (m$^3$/kg)</td>
</tr>
<tr>
<td>$c^\alpha$</td>
<td>mol concentration (mol/m$^3$)</td>
</tr>
<tr>
<td>$C^\alpha$</td>
<td>mass concentration (kg/m$^3$)</td>
</tr>
<tr>
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Appendix B. Relation between the aqueous activity coefficient and the octanol–water distribution coefficient

The aqueous activity coefficient $\zeta_w^\kappa$ can be related to the octanol–water distribution coefficient $K_{ow}^\kappa$ in the following way. We consider the octanol–water mass transfer of component $\kappa$

$$
C_o^\kappa \leftrightarrow C_w^\kappa.
$$

The chemical potential (partial molar free energy) of component $\kappa$ can be evaluated as

$$
\mu_c^\kappa(T,p) = \mu_0(T) + RT\ln(f_c^\kappa/f_0)
$$
and
\[
\mu^K_w(T, p) = \mu^0_\alpha(T) + RT \ln(f^K_w/f^K_\alpha),
\] (B.3)

where \(f^K_\alpha = \gamma^K_\alpha \gamma^K_\alpha\) is the fugacity of component \(\kappa\) in phase \(\alpha\). At thermodynamic equilibrium we have
\[
\mu^K_\alpha = \mu^K_w \Leftrightarrow f^K_\alpha = f^K_w \Leftrightarrow \gamma^K_\alpha \gamma^K_\omega \Leftrightarrow \gamma^K_w \gamma^K_\omega \Leftrightarrow \frac{V^K_\alpha}{V^K_w} = \frac{c^K_\alpha}{c^K_w} = K^K_{ow},
\] (B.4)

where \(V_\alpha\) is the molar volume of phase \(\alpha\). For a less or non-polar component \(\kappa\) we should assume \(\zeta^K_\omega \approx 1\). In this case, the aqueous activity coefficient is directly proportional to the octanol–water distribution coefficient:
\[
\frac{\gamma^K_w}{\gamma^K_\omega} \propto K^K_{ow}.
\] (B.5)

References


