

## TRANSPORT OF VOLATILE CHLORINATED HYDROCARBONS IN UNSATURATED AGGREGATED MEDIA

THOMAS GIMMI<sup>1</sup>, HANNES FLÜHLER<sup>1</sup>, BJØRN STUDER<sup>1</sup>, and ANDERS RASMUSON<sup>2</sup>

<sup>1</sup> *Institute of Terrestrial Ecology, ETH Zürich  
Grabenstrasse 3  
CH - 8952 Schlieren*

<sup>2</sup> *Department of Chemical Engineering Design  
Chalmers University of Technology  
S-41296 Göteborg*

**ABSTRACT.** Transport of volatile hydrocarbons in soils is largely controlled by interactions of vapours with the liquid and solid phase. Sorption on solids of gaseous or dissolved compounds may be important. Since the contact time between a chemical and a specific sorption site can be rather short, kinetic or mass-transfer resistance effects may be relevant.

An existing mathematical model describing advection and diffusion in the gas phase and diffusional transport from the gaseous phase into an intra-aggregate water phase is modified to include linear kinetic sorption on gas-solid and water-solid interfaces. The model accounts for kinetic mass transfer between all three phases in a soil. The solution of the Laplace-transformed equations is inverted numerically.

We performed transient column experiments with 1,1,2-Trichloroethane, Trichloroethylene, and Tetrachloroethylene using air-dry solid and water-saturated porous glass beads. The breakthrough curves were calculated based on independently estimated parameters. The model calculations agree well with experimental data. The different transport behaviour of the three compounds in our system primarily depends on Henry's constants.

### 1. Introduction

Volatile organic chemicals like chlorinated hydrocarbons are commonly used as solvents in various industrial processes or represent precursor compounds, final or waste products in the course of pesticide production. Some of these xenobiotics ultimately accumulate in the atmosphere, unless they undergo degradation. The pathway of such compounds from production to the atmosphere may include soils as an intermediate reservoir. The origin of chlorinated hydrocarbons in soils are dump sites for toxic waste, accidental spills or leakage from storage containments, or intentional use for weed and pest control. Methods for assessing mobility and extractability of such compounds receive considerable attention. This interest is reflected by a number of models describing the transport behaviour of volatile chemicals (e.g. Jury et al., 1983; Enfield et al., 1986; Spencer et al., 1988; Sleep and Sykes, 1989; Jury et al., 1990; Mendoza and Frind, 1990; Shoemaker et al., 1990; Gierke et al., 1992). Most of these models assume equilibrium partitioning between the different phases of the soil. Gierke et al. (1990, 1992) modelled the diffusional transport into the water phase of aggregates explicitly but they assumed instantaneous sorption at the water-solid interface. Sleep and Sykes (1989) considered gas-water partitioning to be a first

order rate process and included dissolution and volatilization of a residual liquid organic phase, but neglected sorption.

The assumption of equilibrium between all phases may not always be justified. The diffusion coefficient of a chemical in the water phase is usually four orders of magnitude smaller than that in the air phase. At relatively large advection velocities in the gas-filled pore space of an aggregated medium, the mean concentration of the water phase will not be in equilibrium with the gas phase concentration, even if equilibration at the gas-liquid interface is instantaneous. Also sorption or desorption processes are reported to happen rather slow in some cases (Estes et al., 1988; Schwarzenbach and Westall, 1981; Wu and Gschwend, 1986). The time scale of phase transfer has to be compared with the contact time given by the time scale of transport within a phase. Large differences may lead to considerable deviations from equilibrium. For estimating earliest possible breakthrough times diffusional transport into a stationary water phase and kinetic sorption behaviour should therefore be explicitly accounted for.

Transport experiments with volatile hydrocarbons are reported by Hutzler et al. (1990), Johnson (1988, cited in Mendoza and Frind [1990]), Spencer et al. (1988), and Gierke et al. (1990, 1992). Such data can usually not be explained by transient model calculations without fitting one or more model parameters to the observed concentrations. The objective of this work was to develop transport experiments in such a way that all parameters needed in the model may be determined a priori. Laboratory experiments were performed with well-defined synthetic aggregates to obtain a data base of transient behaviour of different chlorinated hydrocarbons. The known particle geometry allowed us to obtain independent estimates of these parameters.

## 2. Model Description

Our calculations are based on a model for transport of soluble and hydrolyzable gases in aggregated media presented by Rasmuson et al. (1990). It includes longitudinal convection and dispersion/diffusion in the gas phase as well as lateral diffusive transport towards the centre of water-saturated aggregates. Transport of a liquid organic phase is not regarded. A description of the structure and transport mechanisms is given in Fig. 1. We adapted the model in the following way:

1. If the dissolved vapour of a volatile chlorinated hydrocarbon is not hydrolyzable, only one species exists in solution. The equilibrium at the gas-water interface can be described with Henry's constant  $K_H$  or  $H$ :

$$p = K_H \cdot C_w \quad \text{or} \quad C = H \cdot C_w \quad (1)$$

where  $C_w$  equals the concentration of the chemical in the water phase,  $C$  the gas-phase concentration and  $p$  the partial pressure of the volatile substance (see appendix for dimensions).

2. The mass transfer of a gas across an air-water interface may be limited by a resistance due to a diffusion film either in the liquid or in the gas phase. The gas diffusion film may extend in maximum over the whole macropore radius and lead to a radial concentration gradient. In Rasmuson et al. (1990) it was shown, however, that except for very soluble gases and early times gas-phase resistance is negligible compared to liquid-phase resistance. Therefore, we ignore it and assume a homogeneous concentration over the whole gas-filled cross section.

3. Most organic chemicals exhibit sorption on solids. Two types of linear sorption are known for relatively non polar organic compounds like chlorinated hydrocarbons, depending on the moisture content at the sorption sites (Peterson et al., 1988; Chiou and Shoup, 1985). In

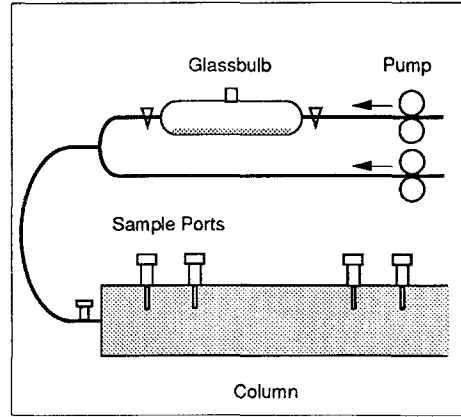
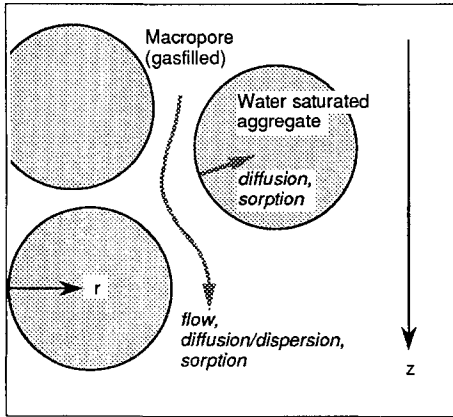


Fig. 1 Principal structure of the aggregated material and transport mechanisms taken into consideration in the model.

Fig. 2 Experimental setup.

completely wet soils, sorption seems to be due to partitioning into the soil organic matter (Karickhoff et al., 1979; Chiou 1989). In unsaturated soils, however, mineral sorption may become important or even dominate the overall sorption (Peterson et al., 1988; Chiou and Shoup, 1985; Ong and Lion, 1991; Estes et al., 1988). Ong and Lion (1991) reported that up to a cover of approximately five monolayers of water the mineral sorption coefficient is very high compared to the water saturated situation. Both types of sorption are found to be time dependent (Schwarzenbach and Westall, 1981; Wu and Gschwend, 1986; Estes et al., 1988). Although it is very likely that this time dependence reflects a transport process – the activation energies for the corresponding mechanisms of sorption are too low to build up a kinetic barrier (Pignatello, 1989) – we included first order kinetic sorption in the model. Two regions with possibly different sorption behaviour because of different water saturation were distinguished: a) the inner, water-saturated region of the aggregate, where presumably organic matter partitioning will take place, and b) the surface of aggregates exposed to the inter-aggregate air, where mineral sorption may dominate. The corresponding equations are

$$(1-\varepsilon_p)\rho_r \frac{\partial C_o}{\partial t} = k_o (\varepsilon_p C_w - (1-\varepsilon_p)\rho_r \frac{C_o}{K_o}) \quad (2)$$

and

$$\frac{(1-\varepsilon_p)\rho_r}{m} \frac{\partial C_m}{\partial t} = k_m (C - \frac{(1-\varepsilon_p)\rho_r}{m} \frac{C_m}{K_m}) \quad (3)$$

where  $C_o$  equals the concentration in the soil organic matter after partitioning from the water phase,  $C_m$  the sorbed concentration at the inter-aggregate sites,  $C_w$  and  $C$  the concentrations in the water and gas phase, respectively,  $\rho_r$  the density of the solid,  $\varepsilon$  and  $\varepsilon_p$  the macropore and aggregate porosity, respectively, and  $m$  equals  $\varepsilon(1-\varepsilon)$ . The equilibrium constants  $K_o$  and  $K_m$  are defined as

$$K_o = \frac{(1-\varepsilon_p)\rho_r}{\varepsilon_p} \frac{C_o}{C_w} \quad \text{and} \quad K_m = \frac{(1-\varepsilon_p)\rho_r}{m} \frac{C_m}{C} \quad (4)$$

The corresponding rate constants  $k_o$  and  $k_m$ , respectively, may be regarded as empirical mass-transfer coefficients rather than as reaction rate constants. In cases where they are large mass-transfer resistance is negligible and equilibrium sorption prevails. Since the model explicitly takes

into account diffusive transport into the water phase of the aggregates, local partitioning into the organic matter may be at equilibrium.

4. The model of Rasmuson et al. (1990) was formulated for the semi-infinite case, i.e. the lower boundary condition was set as  $C(\infty, t) = 0$ . If backward mixing at the outlet end of a finite column is negligible, i.e. for a liquid phase moving or a relatively high column Peclet number, this boundary condition is appropriate for finite length column experiments. If backward mixing occurs, i.e. in a gas diffusion dominated system, however, it will lead to erroneous values near the real column boundary. Therefore, we used  $C(L, t) = C_L$  as lower boundary condition, where  $L$  is the length of the column.

This leads finally to the following set of equations:

(i) *Equation of continuity for gas-filled macropores:*

$$\frac{\partial C}{\partial t} + \frac{(1-\varepsilon_p)\rho_r}{m} \frac{\partial C_m}{\partial t} + V \frac{\partial C}{\partial z} - D_L \frac{\partial^2 C}{\partial z^2} = - \frac{(\alpha_f+1) N_o}{m b} \quad (5)$$

The terms in Eq. (5) describe from left to right: accumulation in macropores, accumulation on solids exposed to inter-aggregate air, convection in gas phase, dispersion in gas phase, and uptake by aggregates.  $V$  is the gas advection velocity in the macropores,  $D_L$  the longitudinal gas-phase dispersion coefficient,  $N_o$  the flux from the macropores into the aggregates,  $b$  the aggregate radius, and  $\alpha_f$  a form factor with a value of 2 for spheres (Rasmuson, 1985).

(ii) *Equation of continuity for water-filled micropores:*

$$\varepsilon_p \frac{\partial C_w}{\partial t} + (1-\varepsilon_p) \rho_r \frac{\partial C_o}{\partial t} = \varepsilon_p D_w \left( \frac{\partial^2 C_w}{\partial r^2} + \frac{\alpha_f}{r} \frac{\partial C_w}{\partial r} \right) \quad (6)$$

The left hand side of Eq. (6) accounts for accumulation in water and solid phase of aggregates, respectively, whereas the right hand side describes diffusional transport into the water phase of the micropores.  $D_w$  is the apparent liquid phase diffusion coefficient.

(iii) *Coupling gas-filled macropores and water-filled micropores:*

$$N_o = \varepsilon_p D_w \left( \frac{\partial C_w}{\partial r} \right)_{r=b} = \frac{\varepsilon_p D_w}{H} \left( \frac{\partial C_p}{\partial r} \right)_{r=b} \quad (7)$$

where  $C_p$  is an equivalent gas-phase concentration.

(iv) *Coupling water-solid and gas-solid interfaces:*

see Eqs. (2) and (3).

The initial and boundary conditions are defined as:

$$C(0, t < t_0) = C_0, \quad C(0, t > t_0) = 0 \quad (8)$$

$$C(L, t) = C_L \quad (9)$$

$$C(z, 0) = C_i \quad (10)$$

$$\frac{\partial C_w}{\partial r}(0, z, t) = 0 \quad (11)$$

$$C_w(r, z, 0) = \frac{C_i}{H} \quad (12)$$

$$C_m(z, 0) = \frac{m}{(1-\epsilon_p)\rho_r} K_m C_i \quad (13)$$

$$C_o(r, z, 0) = \frac{\epsilon_p}{(1-\epsilon_p)\rho_r} \frac{K_o}{H} C_i \quad (14)$$

The analytical solution of a similar system of equations for the semi-infinite case is given in Rasmuson (1985) and Rasmuson et al. (1990). For the calculations of this paper, we inverted the Laplace-transform solution for the finite column numerically with the TALBOT-Routine (Jury and Roth, 1990) to derive the gas phase concentration  $C(z,l)$ .

### 3. Materials and Methods

#### GAS COMPOUNDS

The breakthrough experiments described below were carried out with three chlorinated hydrocarbons, 1,1,2-Trichloroethane (T112), Trichloroethylene (TRI) and Tetrachloroethylene (PER), respectively. Their chemical properties are given in Table 1. The range of their Henry's constants reported in the literature is remarkably wide.

#### EXPERIMENTAL SETUP (Fig. 2)

A glass bulb contained small amounts of all three liquid hydrocarbons. Air was pumped through the bulb at a constant rate and thereby saturated. At the outlet of the bulb, the gas concentration was adjusted by diluting the gas stream with air. The flow rate  $Q$  was measured with a soap film flow meter. A sample port mounted on the connection between the bulb and the column allowed the measurement of the inlet concentration. The plexiglass column was 6 cm in diameter and 50 cm long. Gas samples were obtained through four sample ports at 5, 10, 40, and 45 cm from the inlet of the column. The needle of the sampling syringe was inserted through a Teflon coated septum

**Table 1** Chemical properties of the volatile chlorinated hydrocarbons. Density, solubility, vapour pressure and the Henry's constant  $H$  are given for 20 °C.

	1,1,2- Trichloroethane	Trichloroethylene	Tetrachloroethylene
Abbreviation	T112	TRI	PER
Molecular weight	133.4	131.4	165.8
Boiling point [°C]	113.8 <sup>¶</sup>	87.0 <sup>¶</sup>	121.0 <sup>¶</sup>
Density [kg m <sup>-3</sup> ]	1.434·10 <sup>3</sup> <sup>¶</sup>	1.464·10 <sup>3</sup> <sup>¶</sup>	1.623·10 <sup>3</sup> <sup>¶</sup>
Solubility [kg m <sup>-3</sup> ]	4.42 - 4.5 <sup>†</sup>	1.0 - 1.1 <sup>†</sup>	0.12 - 0.15 <sup>†</sup> , 0.4 <sup>#</sup>
Vapour pressure [kPa]	3.3 - 4.04 <sup>†</sup>	7.86 - 9.87 <sup>†</sup>	1.8 - 2.48 <sup>†</sup>
H (range/values used)	0.03 - 0.37 <sup>†</sup> / 0.04	0.30 - 0.53 <sup>§,†,‡</sup> / 0.30 <sup>§</sup>	0.35 - 1.2 <sup>#,†</sup> / 0.55 <sup>§</sup>

<sup>§</sup> Gossett (1987); <sup>¶</sup> Handbook of Chemistry and Physics (1983-84); <sup>#</sup> Lyman et al. (1982); <sup>†</sup> Mackay and Shiu (1981); <sup>‡</sup> Munz and Roberts (1987)

and a capillary. The needle tip reached the end of the capillary which protruded 2 cm into the porous column material. The outlet end of the column was covered with a nylon screen (open mesh width 1 mm) to keep the glass beads in place.

#### GAS SORPTION BY EXPERIMENTAL EQUIPMENT

The three volatile substances T112, TRI, and PER exhibit a high affinity for certain polymer materials produced from halogenated hydrocarbons. Sorption by materials used in the construction of the apparatus was tested in a semi-quantitative manner by enclosing pieces of different materials in a chamber (35 ml) and exposing them to an initial concentration of  $5.8 \text{ mmol m}^{-3}$  T112,  $1.4 \text{ mmol m}^{-3}$  TRI, and  $2.3 \text{ mmol m}^{-3}$  PER. Trace gas disappearance during the first five hours was used for a relative rating of sorption. Nitril O-rings drastically reduced the T112 concentration by 90%, PER by 80% and TRI by 70%. Sorption by Viton materials (tubing and O-rings) was slight but still detectable. Sorption by the materials ultimately used in the experiment, i.e. by plexiglass, Teflon slabs, and Teflon coated O-rings was not detectable. However, desorption from the exposed plexiglass and Teflon pieces placed into a chamber with clean air was detectable but the concentrations measured after five hours were very low. Based on these tests the sink/source behaviour of the experimental material is considered to be negligible in this context. Nevertheless, glass was preferentially used for highly exposed surfaces and exposure of Teflon surfaces was minimized.

#### GAS ANALYSIS

Immediately after obtaining a gas sample of 5  $\mu\text{l}$  it was injected into a gaschromatograph (on-column) and analyzed with a  $^{63}\text{Ni}$  electron capture detector. Due to the short delay (seconds) between sampling and injection the sample size could be kept small.

#### POROUS MEDIA

We used two types of spherical glass beads both with diameters ranging from 2 to 3 mm. The water-saturated, porous glass beads (SIRAN, Schott Mainz, FRG) are an idealized physical analogue of an aggregated soil with an air-filled inter- and a water-filled intra-aggregate pore space. The porosity of the SIRAN beads is approximately 0.60. The diameter of most pores determined with mercury porosimetry is in the range of 10 to 20  $\mu\text{m}$ . The solid (non-porous) glass beads, on the other hand, represent a porous bed with the same macroporosity but without any intra-aggregate pore space, i.e. no micropores.

## 4. Experiments

#### EXPERIMENTAL PROCEDURE

We performed two experiments with different porous media, and different gas flow velocities, and initial and inlet boundary conditions. In both cases the outlet end of the column was kept open to the atmosphere during the experiment, which resulted in a lower boundary concentration  $C_L \approx 0$  for  $t > 0$ . The ambient temperature was 25°C.

In Experiment A, the dry, non porous glass beads were used. It was carried out at a flow rate of  $Q = 1.43 \cdot 10^{-7} \text{ m}^3 \text{ s}^{-1}$ . The average convection velocity was  $V = Q \cdot (\epsilon A)^{-1} = 1.28 \cdot 10^{-4} \text{ m s}^{-1}$ , where  $\epsilon$  is the air filled porosity ( $\epsilon = 0.40$ ) and  $A$  the column cross section. The column was initially free from T112, TRI, and PER ( $C_i = 0$ ). The input concentration  $C_0$  for a pulse duration

of 59 min was  $1.22 \cdot 10^{-1} \text{ mol m}^{-3}$  for T112,  $5.75 \cdot 10^{-1} \text{ mol m}^{-3}$  for TRI, and  $5.13 \cdot 10^{-2} \text{ mol m}^{-3}$  for PER. Then,  $C_0$  was kept zero. The breakthrough of the volatile compounds in the gas phase was measured at 10 cm and 40 cm from the inlet.

Experiment B was performed with water-saturated porous glass beads. The porous particles were saturated under vacuum. During the filling procedure of the column the excess water in the large pores between the particles was drained. The water content remained nearly constant during the experiment (less than 1% change). Prior to the experiment the outlet end was closed for equilibration with a small amount of T112, TRI, and PER, resulting in constant initial concentrations  $C_i = 5.69 \cdot 10^{-5} \text{ mol m}^{-3}$  (T112),  $9.21 \cdot 10^{-3} \text{ mol m}^{-3}$  (TRI), and  $5.13 \cdot 10^{-4} \text{ mol m}^{-3}$  (PER), throughout the column. Thereafter the column was flushed with clean air ( $C_0 = 0$ ) at a flow rate  $Q$  of  $8.20 \cdot 10^{-8} \text{ m}^3 \text{ s}^{-1}$ , which led to an average convection velocity of  $6.53 \cdot 10^{-5} \text{ m s}^{-1}$  ( $\varepsilon = 0.44$ ). At 40 cm from the inlet, i.e. 10 cm from the outlet end, the concentration decrease was measured.

#### INDEPENDENT ESTIMATION OF MODEL PARAMETERS

Every transport model introduces a given number of parameters. If model calculations and experimental values are compared to test the mechanistic model assumptions, the parameters must be independently determined. In this model three categories of parameters are needed, namely transport, chemical, and structure parameters.

##### (i) Structure Parameters:

The model parameters describing the structure of the medium are the inter-aggregate or macropore porosity,  $\varepsilon$ , the porosity of the individual particles,  $\varepsilon_p$ , as well as their radius or half width,  $b$ . The porosities may be calculated from the solid density,  $\rho_r$ , the apparent particle density,  $\rho_p$ , and the apparent density of the entire dry column filling,  $\rho_a$ :

$$\varepsilon = 1 - (\rho_a/\rho_p) \quad (15)$$

$$\varepsilon_p = 1 - (\rho_p/\rho_r) \quad (16)$$

Material density  $\rho_r$  was determined with pycnometers. Apparent density  $\rho_a$  was calculated after drying of the column filling. Apparent particle density  $\rho_p$  was determined by embedding the porous particles in a fine sand mixture (0.3 - 0.4 mm) with the smallest sand particles larger than the largest pores of the particle ( $< 0.3 \text{ mm}$ ). The water content of the column was determined by weighing and turned out to be slightly lower than the value corresponding to the intra-particle porosity (90% saturation). The part of the aggregates not saturated with water was considered to belong to the inter-aggregate porosity. The effective diffusion radius of the aggregates,  $b$ , was estimated from the mean mass of one particle and the water saturation, assuming spherical shape.

For the porous material  $\rho_r$  is  $2.50 \cdot 10^3 \text{ kg m}^{-3}$  and  $\rho_p$   $9.97 \cdot 10^2 \text{ kg m}^{-3}$ , whereas for the non porous glass beads  $\rho_r$  and  $\rho_p$  are identical and equal  $2.83 \cdot 10^3 \text{ kg m}^{-3}$ . The values of the structure parameters are specified for each experiment in Table 2.

##### (ii) Chemical Parameters:

Equilibrium partitioning coefficients between the three phases water, air and solid, as well as mass-transfer coefficients for solute-solid and vapour-solid interactions are needed. The range of values for Henry's constants found in the literature and the most trustworthy values used in the calculations are listed in Table 1. Finding data describing the solute-solid and vapour-solid interactions is more difficult. The solute-solid partitioning coefficients can be estimated based on the organic carbon content of the soil and the chemical's octanol-water partition coefficient (Karickhoff

et al., 1979, Schwarzenbach and Westall, 1981). The mass-transfer coefficients as well as the vapour-solid equilibrium constants which are controlled by the soil minerals (Chiou and Shoup, 1985) must be determined experimentally. In our case, neither glass material sorbed the chemicals used. Therefore the equilibrium and mass-transfer coefficients were set to zero.

*(iii) Transport Parameters:*

Eqs. (5) and (6) introduced the average flow velocity  $V$ , the longitudinal dispersion coefficient  $D_L$ , and  $D_w$ , the apparent diffusion coefficient in water.  $V$  is given by the flow rate  $Q$ , as mentioned.  $D_L$  describes mixing within the air-filled inter-aggregate pore space. For low convective velocities, such as in our experiments, dispersion in the gas phase is dominated by molecular diffusion (Fried and Combarous, 1971).  $D_L$  is replaced therefore by  $D_a$ , the apparent diffusion coefficient of the air phase. Hence, we may estimate  $D_a$  in the same way as  $D_w$ , namely based on the molecular diffusion coefficients,  $D_a^\circ$  and  $D_w^\circ$ , of the considered compounds in free air and water, as tabulated in handbooks, and the inter- and intra-aggregate tortuosities  $\tau_a$  and  $\tau_w$ , respectively:

$$D_a = D_a^\circ \cdot \tau_a^{-1} \quad (17)$$

$$D_w = D_w^\circ \cdot \tau_w^{-1} \quad (18)$$

In Table 3 the values of  $D_a^\circ$  and  $D_w^\circ$  are given. The tortuosities describe structural transmission properties such as phase continuity, connectivity, and tortuous path lengths. These parameters can be quite reliably estimated provided the volumetric portion of the phase is not too small (cf. reviews by Van Brakel and Heertjes, 1974, and Troch et al., 1982). Especially the expression for gases in non-aggregated media derived by Millington (1959)<sup>1</sup>

$$D = D^\circ \cdot \epsilon^{7/3} \cdot E^{-2} \quad (19)$$

where  $\epsilon$  is the air filled and  $E$  the total porosity, has proven to be suitable in the crucial range of low air contents (Collin and Rasmuson, 1988). This expression used for unsaturated materials yields

$$\tau_a = \left(\frac{E}{\epsilon}\right)^2 \cdot \epsilon^{-1/3} \quad (20)$$

which simplifies to

$$\tau_a = \epsilon^{-1/3} \quad (21)$$

for air dry material. For completely saturated materials  $\epsilon$  in Eq. (21) may be replaced by the volumetric water content  $\theta$  to calculate  $\tau_w$ .

To determine the tortuosity of the inter-aggregate air phase we conducted an independent  $\text{CO}_2$  diffusion experiment using an other column of 20 cm length filled with air-dry solid glass beads. After a step change of the  $\text{CO}_2$  concentration at the inlet the change of the  $\text{CO}_2$  partial pressure within the column caused by diffusion was measured with a  $\text{CO}_2$  electrode. In this experiment all parameters but the tortuosity factor were known. By comparison of measured concentrations with those calculated by means of the known analytical solution the effective diffusion coefficient and thus the tortuosity was estimated. The result was used for model calculations in Experiment A as well as in Experiment B.

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<sup>1</sup>  $\epsilon$  is raised to a power of 7/3 instead of 10/3 as reported by Millington (1959), because he included the gas filled area in the accumulation term of the diffusion equation.



In a similar way, the tortuosity of the water phase within the aggregates was determined with chloride. Porous glass particles were saturated with a KCl solution and at time zero placed in a stirred solution containing a low KCl concentration. The increase of the chloride concentration in solution was measured with a chloride electrode. Again, comparing measurements with a known analytical solution of spherical diffusion yields the effective diffusion coefficient and hence the tortuosity of the water phase in the particles, which was later used in the model calculation. In Table 4 the results of the tortuosity determinations are listed, together with some calculated values for comparison. Macropore tortuosities calculated using Eq. (21) give reasonable values, whereas the micropore tortuosity of the SIRAN particles is underestimated compared to the experimentally determined value.

**Table 2** Structure parameters for the experiments with dry, non porous (A) and with water-saturated, porous glass beads (B), respectively. The values for aggregate water saturation and total porosity are included as illustration, but they are not needed as input.

	Experiment A	Experiment B
Macropore porosity, $\epsilon$	0.40	0.44
Aggregate porosity, $\epsilon_p$	0	0.60
Aggregate water saturation, $s_p$	–	0.90
Total porosity, E	0.40	0.76
Aggregate diffusion radius, b [m]	--	$1.12 \cdot 10^{-3}$

**Table 3** Transport and chemical parameters for the experiments with dry, non porous (Experiment A) and with water-saturated, porous glass beads (Experiment B). T = 25 °C.

	T112	TRI	PER
$D_a^o$ [ $m^2 s^{-1}$ ]	$7.9 \cdot 10^{-6}$ §	$8.8 \cdot 10^{-6}$ §	$8.0 \cdot 10^{-6}$ §
$\tau_a$	1.47		
$D_w^o$ [ $m^2 s^{-1}$ ]	$9.3 \cdot 10^{-10}$ ¶	$9.6 \cdot 10^{-10}$ ¶	$8.7 \cdot 10^{-10}$ ¶
$\tau_w$	1.77		
V [ $m s^{-1}$ ]	$1.28 \cdot 10^{-4}$ (Experiment A) / $6.53 \cdot 10^{-5}$ (Experiment B)		
H [dim.less]	0.05	0.33	0.61
$K_m$ [dim.less]	0		
$K_o$ [dim.less]	0		

§ Pannwitz (1985); ¶ Hayduk and Laudie (1974)

**Table 4** Measured and estimated tortuosities  $\tau$  for the different pore spaces.

	Macropores, Experiment A/B	Micropores, Experiment B
$\tau$ measured	$\tau_a = 1.47$	$\tau_w = 1.77$
$\tau$ calculated, Eq. (21)	$\tau_a = 1.36^{\S} / \tau_a = 1.31^{\P}$	$\tau_w = 1.19^{\#}$

$^{\S} \epsilon = 0.40$ ;  $^{\P} \epsilon = 0.44$ ;  $^{\#} \epsilon_p = 0.60$

## 5. Results and Discussion

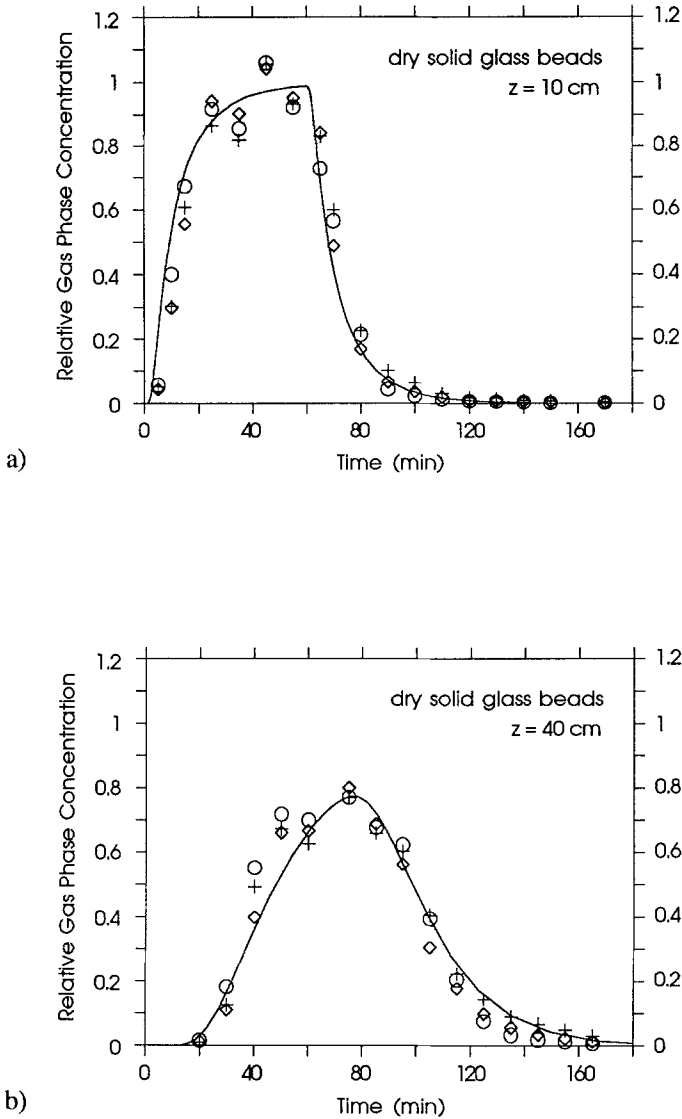
The results of experiment A with the dry solid glass beads are depicted in Fig. 3 a and b. The breakthrough of 1,1,2-Trichloroethane (T112), Trichloroethylene (TRI) and Tetrachloroethylene (PER) in a distance 10 cm from the inlet (a) and 40 cm from the inlet (b) is shown, respectively. As can be expected for a dry, non-sorbing medium, the vapours of all three chlorinated hydrocarbons show more or less the same breakthrough behaviour. The solid line refers to the model calculations for T112, TRI and PER based on independently estimated parameters. The differences in the gaseous diffusion coefficients for the three compounds are very small and the three modelled curves coincide. The parameters used for these calculations are listed in Table 2 and 3.

The identical behaviour of the three vapours and the good agreement between calculations and measurements in the dry case illustrate that the assumption of no sorption by the column as well as the filling material is justified. It is especially noteworthy that at a distance of 10 cm the coincidence is as good as at 40 cm, without adjustment of any parameter.

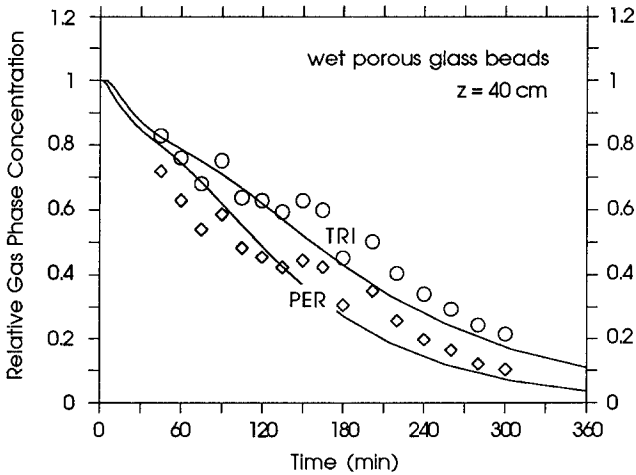
Fig. 4 (TRI, PER) and 5 (T112) show the results of experiment B with the porous, water-saturated SIRAN particles. The measurements are made at a distance of 40 cm from the inlet. Again, the model calculations (solid lines) are based on the independently determined parameters as listed in Table 2 and 3.

The concentration decrease is fastest for PER (Fig. 4) and very slow for T112 (Fig. 5), as expected from Henry's constants. The agreement between calculations and measurements is good for PER and TRI, whereas the T112 data show a large scatter but seem to decrease faster than predicted. There is, however, an uncertainty in the calculations due to the uncertainty in the parameter values, Henry's constants especially having a big influence on the calculated breakthrough curves. The values for T112 which are found in the literature vary considerably (cf. Table 1). In Fig. 5 the measured data of T112 are graphed together with the corresponding calculations for the minimum and maximum Henry's constants (dashed lines), which embrace the shaded area. It shows that the deviations between measurements and the calculation using the parameters in Table 2 and 3 (solid line) might be attributed to a different Henry's constant.

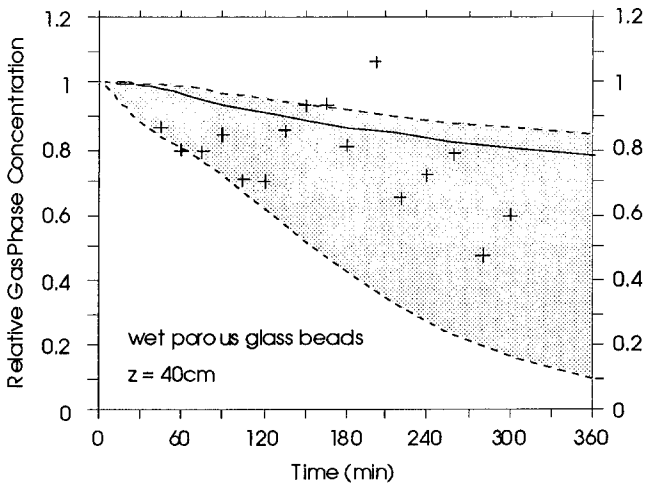
Measurement errors guessed from uncertainties in the initial concentration and in the calibration curve are for both experiments approximately  $\pm 10\%$  for TRI and PER and  $\pm 15\%$  for T112. The small sample size (5  $\mu\text{l}$ ) minimized disturbances of the gas phase, but it produced a sample that was not averaged over the whole cross section of the column. This may have contributed to the scatter of gas concentration data. In general, concentrations measured in gas samples collected and



**Fig. 3a and b** Experiment A: Breakthrough curves of Trichloroethylene (o), Tetrachloroethylene (◊) and 1,1,2-Trichloroethane (+) through the dry, non aggregated medium at a distance of 10 cm (a) and 40 cm (b) from the inlet. The solid lines represent independent calculations. The pulse injected had a velocity of  $1.28 \cdot 10^{-4} \text{ m s}^{-1}$  and a duration of 59 min. The other experimental parameters are listed in Table 2 and 3. Measurement errors guessed from uncertainties in input concentration and in the calibration curve are approximately  $\pm 10\%$  for TRI and PER and  $\pm 15\%$  for T112.



**Fig. 4** Experiment B: Concentration decrease of Trichloroethylene (o) and Tetrachloroethylene (◊) at a distance of 40 cm from the inlet, i.e. at 10 cm from the outlet. The solid lines represent independent calculations. The column contains porous, water-saturated particles. It was previously saturated with VOC's and then flushed with clean air. The average flow velocity was  $6.53 \cdot 10^{-5} \text{ m s}^{-1}$ . The other parameters are listed in Table 2 and 3. The guessed measurement errors are approximately  $\pm 10\%$  (TRI and PER).



**Fig. 5** Experiment B: Concentration decrease of 1,1,2-Trichloroethane (+) at a distance of 40 cm from the inlet, i.e. at 10 cm from the outlet, for the same experimental conditions as stated in Fig. 4. The solid line represents the independent calculation. The shaded area embraces the calculations using the minimum and maximum Henry's constants found in the literature. The guessed measurement errors for T112 are approximately  $\pm 15\%$ .

transferred with syringes are more variable than those measured in liquid samples, not only because of gas losses or sorption/desorption between sampling and injection time but also because of possible variations of total pressure within the syringe.

The experiments illustrate that for a wet, non-sorbing medium the Henry's constants are very important with respect to the breakthrough behaviour. For real soils, the effect of the Henry's constant will be superimposed on sorption properties. For some volatile compounds, vapour-solid and solute-solid sorption coefficients and the corresponding rates may be dominant or at least as important as the air-water distribution ratio, since most of these volatile chemicals are not very soluble, but some show a strong affinity for organic material.

## 6. Conclusions

The experiments with the three chlorinated hydrocarbons mimic a situation where organic liquids exist as immobile insular pockets in a porous body acting as sources of the corresponding vapours. The mechanisms controlling the spreading of the gaseous constituents are gas diffusion and convection, dissolution in the aqueous phase, and transport to sorptive sites. The experiments showed that in a wet, aggregated medium having no solid phase sorption capacity, the transport behaviour of vapours of chlorinated hydrocarbons is dominated by the Henry's constants. This entails the question, whether Henry's constants are identical for pore water of a soil as well as for bulk distilled water usually reported in tables.

Calculations for finite column experiments are made with an adaption of the model of Rasmuson et al. (1990) using independently estimated parameters. They correspond well with the measurements, both for dry, non aggregated, non sorbing as well as for wet, aggregated, non sorbing media. Further possibly relevant descriptive capabilities of the model such as rate-dependent multi-site sorption (e.g. at the solid-water and the solid-gas interface) could not be tested with this data base. The next step will be to use real soil aggregates to explore the kinetic control of retardation mechanisms.

### Appendix: Notation List and Units

$b$	aggregate radius, m
$C$	concentration in gas-filled macropores, $\text{mol m}^{-3}$ (= mM)
$C_m$	sorbed concentration at the inter-aggregate sites, $\text{mol kg}^{-1}$ dry solid
$C_o$	concentration in the soil organic matter after partitioning with the water phase, $\text{mol kg}^{-1}$ dry solid
$C_p$	concentration in water-filled micropores expressed as an equivalent gas phase concentration (Eq. (7)), $\text{mol m}^{-3}$
$C_w$	concentration in the water phase, $\text{mol m}^{-3}$
$D$	apparent diffusivity in a porous medium (Eq. (19)), $\text{m}^2 \text{s}^{-1}$
$D_a$	apparent diffusivity in gas-filled macropores, $\text{m}^2 \text{s}^{-1}$
$D_a^\circ$	molecular diffusivity in free air, $\text{m}^2 \text{s}^{-1}$
$D_L$	dispersion coefficient in gas-filled macropores, tortuosity and constrictivity included, $\text{m}^2 \text{s}^{-1}$
$D^\circ$	molecular diffusivity (Eq. (19)), $\text{m}^2 \text{s}^{-1}$
$D_w$	apparent diffusivity in water-filled micropores, $\text{m}^2 \text{s}^{-1}$
$D_w^\circ$	molecular diffusivity in free water, $\text{m}^2 \text{s}^{-1}$
$H$	Henry's constant, dimensionless
$K_H$	Henry's constant, $\text{Pa} (\text{mol m}^{-3})^{-1}$
$K_m$	Equilibrium constant for vapour sorption, dim.less

$k_m$	mass-transfer coefficient for vapour sorption, $s^{-1}$
$K_o$	Equilibrium constant for solute sorption, dim.less
$k_o$	mass-transfer coefficient for solute sorption, $s^{-1}$
$L$	column length, m
$m$	$= \epsilon/(1-\epsilon)$
$N_o$	flux from macropores to aggregates, $mol\ m^{-2}\ s^{-1}$
$p$	partial pressure, Pa
$r$	radial distance from centre of aggregate, m
$t$	time, s
$V$	average gas velocity in the macropores, $m\ s^{-1}$
$z$	distance along macropore, m
$\alpha_f$	form factor with a value of 2 for spheres
$\epsilon$	macropore porosity
$\epsilon_p$	aggregate porosity
$\rho_a$	apparent density, $kg\ m^{-3}$
$\rho_p$	apparent particle density, $kg\ m^{-3}$
$\rho_r$	solid density, $kg\ m^{-3}$
$\tau_a$	tortuosity of the gas-filled macropores
$\tau_w$	tortuosity of the water-filled aggregates

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