

Supplementary Material

1 WATER VAPOR PRESSURE

The vapor pressure of the water component in the presence of capillary effect is regulated by the Kelvin equation (Bourgeat et al., 2008; Huang et al., 2017)

$$P_{vap} = P_{sat} \exp \left(-\frac{P_{cap}}{N_L RT} \right) \quad (S1)$$

in which P_{sat} indicates the saturated vapor pressure of pure water (Bourgeat et al., 2008)

$$P_{sat}(T) = P_0 \exp \left[\left(\frac{1}{T_0} - \frac{1}{T} \right) \frac{h_{\Delta e} M_w}{R} \right]. \quad (S2)$$

Equation (S2) is also known as Clausius-Clapeyron equation where $T_0 = 373$ K, $P_0 = 101,325$ Pa and $h_{\Delta e}$ denotes the latent heat of water vaporization.

2 MODEL VALIDATION FOR TCE TRANSPORT

McCarthy and Johnson (1993) conducted a detailed experiment (the M&J experiment) where they injected TCE-saturated aqueous solution into a 1-m scale aquifer model and measured the steady-state TCE concentrations in the groundwater and in gas phase. Following the same scenario, Atteia and Höhener (2010) proposed a semianalytical model (the A&H model) predicting the vertical concentration profile of a volatile organic contaminant (VOC) in variably-saturated homogeneous soil.

Here, we construct a 1D numerical model to mimic the M&J experiment and compare our simulation results with the experimental data and the A&H model. The parameters of the M&J experiment are listed in Table S1. We first use the van Genuchten model to fit the measured soil water retention curve (Fig. S1(a)). Next, we use the vertical dispersivity α_z of the sand as a fitting parameter following Atteia and Höhener (2010). As a result, we found a dispersivity value of 0.9 mm as the “best fit” for the vertical profile of gaseous TCE (see Fig. S1(b)). This value is similar to the fitted value of 1 mm given by Atteia and Höhener (2010) and represents approximately the main grain size of the sand. Overall, an excellent agreement was obtained between the numerical simulation and experimental data/semianalytical solution. Thus, the accuracy of the numerical model in simulating VOC transport in a variably-saturated porous medium is validated.

Table S1. Parameters of the McCarthy and Johnson experiment.

Parameter	Value	Unit
Diffusion coefficient in free gas, D_{0a}	8.3×10^{-6}	$\text{m}^2 \text{s}^{-1}$
Diffusion coefficient in free water, D_{0w}	9.1×10^{-10}	$\text{m}^2 \text{s}^{-1}$
Henry's Law constant, H	1.062×10^{-3}	$\text{mol m}^{-3} \text{Pa}^{-1}$
Groundwater velocity, v	0.1	m d^{-1}
Porosity, ϕ	0.38	-
Residual saturation, S_r	0	-
van Genuchten parameter, α_{vG}	0.06	cm^{-1}
van Genuchten parameter, m_{vG}	0.8	-

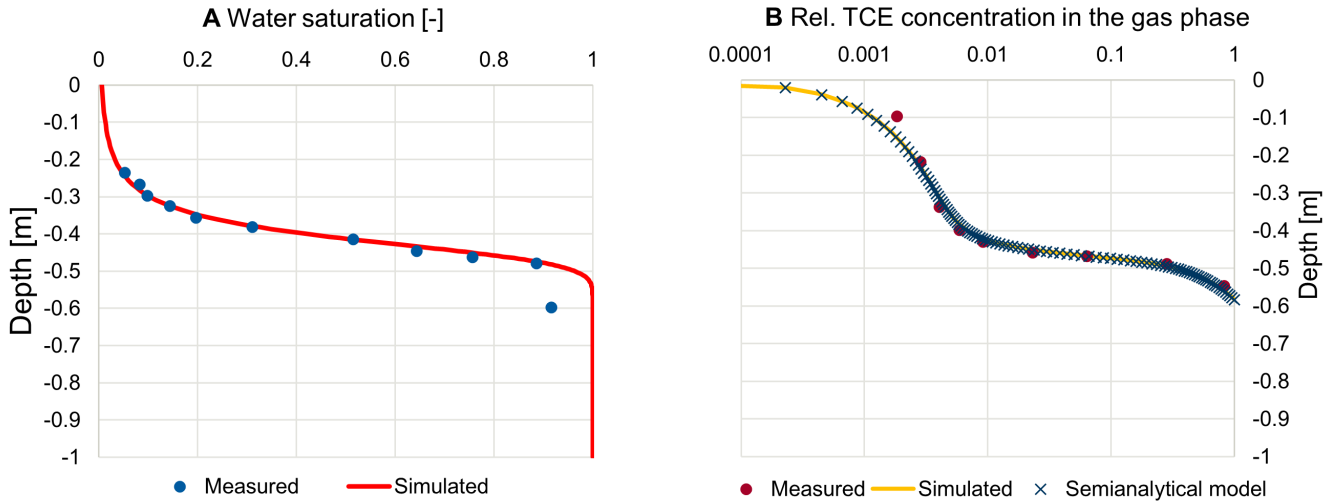


Figure S1. (A) Experimental and model-fitted soil water retention curves; (B) relative TCE content in the gas phase: experimental data, semianalytical model and fitted simulation results.

3 VERTICAL MASS TRANSFER OF TCE IN A VARIABLY-SATURATED POROUS MEDIUM

In the unsaturated zone, transport of TCE takes effect by both diffusion and dispersion in the liquid phase and primarily diffusion in the gas phase. Hence, the total dispersive flux of TCE in the vertical direction (m s^{-1}) can be expressed as (Atteia and Höhener, 2010)

$$\mathbf{J}_{tot}^c = - \left[\phi^{\frac{4}{3}} (1 - S_L)^{\frac{10}{3}} D_G^c + \frac{P_G \left(\phi^{\frac{4}{3}} S_L^{\frac{10}{3}} D_L^c + \alpha_v k_{rL} q_{0L} \right)}{N_L H} \right] \frac{dx_G^c}{dz} = -f(z) \frac{dx_G^c}{dz} \quad (\text{S3})$$

where q_{0L} is the groundwater flow velocity in the saturated zone and $f(z)$ represents the depth-dependent overall dispersive effect. In Table S2, we select two points A and B above the water table and calculate their overall diffusion coefficients $f(z)$.

Table S2. Depth-dependent calculation of $f(z)$.

Point	A	B
Distance above water table (m)	0.16	4.0
Gas pressure, P_G (Pa)	101325	101325
Water saturation, S_L (-)	0.997	0.223
Relative permeability, k_{rL} (-)	0.969	0
$f(z)$ ($\text{m}^2 \text{s}^{-1}$)	1.87e-8	8.36e-7

It can be seen that the overall dispersive coefficient $f(z)$ of Point B is almost 45 times larger than Point A. Since at steady state the total dispersive flux in Eq. (S3) should be independent of the depth, it follows that the gradient of gas phase molar fraction $\frac{dx_G^c}{dz}$ is 45 times larger at Point A compared to B (see **Figure 3C**).

REFERENCES

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