

1 Mass Transport in Partially Saturated Porous Media

The vadose zone is a three-phase system and thus any chemical specie is distributed between these three phases. However, the mass transport still only occur through the gas and liquid phases of the system, therefore the transport of the *total* concentration c_T is due to diffusive and advective transport in these phases.

$$\frac{\partial c_T}{\partial t} = \nabla[D_w\theta_w\tau_w\nabla c_w + D_g\theta_g\tau_g\nabla c_g] - \nabla(v_w\theta_w c_w + v_g\theta_g c_g) \quad (1)$$

Here D_w and D_g are the water and gas diffusion constants respectively; θ_w and θ_g are the water and gas filled porosities; τ_w and τ_g are the tortuosity, correcting for diffusivity in porous media; v_w and v_g are the water and gas velocity; finally c_w and c_g are the water and gas phase concentrations.

As stated above, the total concentration is distributed across the three phases.

$$c_T = \theta_w c_w + c_g \theta_g + c_s \rho_b \quad (2)$$

Where the first and second terms correspond to the water and gas concentrations; the third correspond to the sorbed concentration, where c_s is the sorbed concentration by mass and ρ_b is the soil bulk density. In order to solve (1) we need to state everything in terms of one dependent variable, which we will see is the water concentration c_w .

From Henry's Law we know that a gas concentration is proportional to the water concentration via the eponymous constant H .

$$c_g = H c_w \quad (3)$$

By assuming linear sorption we can describe the sorbed concentration as

$$c_s = \begin{cases} K_p c_w & \text{Water phase sorption} \\ K_p c_g = K_p H c_w & \text{Gas phase sorption} \end{cases} \quad (4)$$

where K_p is the sorption isotherm. For simplicity we will here assume water phase sorption.

Using this we can restate c_T is terms of the water phase concentration.

$$c_T = (\theta_w + \theta_g H + K_p \rho_b) c_w = R c_w \quad (5)$$

The *retardation factor* R is introduced to simplify writing.

Now we substitute all of this in (1).

$$R \frac{\partial c_w}{\partial t} = \nabla[(D_w\theta_w\tau_w + D_g\theta_g\tau_g H)\nabla c_w] - \nabla[(v_w\theta_w + v_g\theta_g H)c_w] \quad (6)$$

Here we recognize that $(D_w\theta_w\tau_w + D_g\theta_g\tau_g H)$ is the effective diffusivity D_{eff} , which gives the final expression

$$R \frac{\partial c_w}{\partial t} = \nabla[D_{\text{eff}}\nabla c_w] - \nabla[(v_w\theta_w + v_g\theta_g H)c_w] \quad (7)$$

Most soil-physics books are concerned with water moving in porous media, with the gas assumed to be immobile and occupy small pockets in the porous media. In this case $v_g = 0$, dropping that term which gives

$$R \frac{\partial c_w}{\partial t} = \nabla[D_{\text{eff}} \nabla c_w] - \nabla[v_w \theta_w c_w] \quad (8)$$

This is the most common form found of the governing equation for mass transport in partially saturated porous media, and the equation that COMSOL solves.

Obviously this does not quite describe the vapor intrusion scenario, where we are concerned with a mobile gas phase and a stationary water phase. Although, this does not necessarily have to be the case, and we could in theory keep both velocity fields if we were interested in such a problem. Regardless, for most of our applications we assume that the soil water is stationary $v_w = 0$ leading to

$$R \frac{\partial c_w}{\partial t} = \nabla[D_{\text{eff}} \nabla c_w] - \nabla[v_g \theta_g H c_w] \quad (9)$$

The implications of this is that we must multiply the gas velocity field with the Henry's Law constant to correctly reflect the transport problem.

Another implication is that **we must set all our boundary conditions in terms of the water phase concentration c_w** . So for one, the concentration boundary condition at the groundwater source must be the groundwater *water* concentration, and not the typical one where we multiply it by H ; as we've seen, this previous correction is built into the governing equation.

The crack entry flux j_{ck} must also be adjusted. This one is a bit trickier though, since we're only concerned the gas phase concentration entering through the crack. Thus it must be stated as a function of the gas phase concentration, i.e. $j_{ck} = f(c_g)$ and this is the contaminant flux that enters the overlying building. But since we must state every boundary condition in terms of c_w , we must scale the boundary condition in the model using Henry's Law as well, and thus it should be j_{ck}/H .