EFFECT OF DISPERSION COEFFICIENT ON NAPL/GAS MASS TRANSFER COEFFICIENT DETERMINATION

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Abstract

Organic pollutants are one of the main pollutants in soils. To evaluate pollutant propagation and to apply a remediation technology, it is necessary to know transfer parameters between pollutant and soil components. Evaporation of the Non Aqueous Phase Liquid "NAPL" is one of the main phenomenon, studied mainly when the Soil Vapor Extraction is used. NAPL/gas mass transfer coefficient is the parameter describing this evaporation phenomenon. Many relations are defined to determine this coefficient with neglecting the dispersion coefficient. In this paper, empirical models for determination of NAPL/gas lumped mass transfer coefficient "λ" from literature are tested. Results are compared to analytical solution of the convection dispersion equation results. The influence of the longitudinal dispersivity α_L on λ determination was evaluated. It has been shown that dispersion coefficient can be neglected in the model of λ determination for pore's velocity more than 0.1 cm·s^{-1}. The correction is need for low pore's velocity.

Key words : *porous media, NAPL/gas mass transfer coefficient, longitudinal dispersivity.*

Introduction

Soil vapor extraction (SVE) is a physical treatment process for in situ remediation of volatile contaminants in vadose zone soils. In this technology, a vacuum is applied to the soil to induce the controlled flow of air and remove volatile and some semi-volatile contaminants from the soil. In this zone, the pollutants are in various forms: dissolved in the residual saturation water, adsorbed on the organic matter and/or clay fraction of the soil, evaporated in gas phase and free in Non-Aqueous Phase liquid (NAPL). At this zone, the NAPL and the aqueous phase are considered not mobile under pressure gradient. When soil gas concentration decreases, the local chemical equilibrium is perturbed, causing the transfer of volatile oil from NAPL phase into the soil gas, where it can be removed. The used model to simulate the transfer between NAPL and gas phase in one-dimension is the mass conservation equation for gas phase (equation [1]).

$$\varphi\, S_g\, \frac{\partial C_{g,\beta}}{\partial t} + q_g\, \frac{\partial C_{g,\beta}}{\partial x} - \varphi\, S_g\, \overline{\overline{D}}_{g,\beta.}\, \frac{\partial^2 C_{g,\beta}}{\partial x^2} = \varphi\, S_g\, \lambda_{o-g,\beta}\, (C_{g,\beta}^{sat} - C_{g,\beta}) \qquad [1]$$

Where t is the time [T], x is the direction [L] φ is the porosity [-], S_g is the *gas* phase saturation [-], q_g is the Darcy's velocity in gas phase [M·T^{-1}], $\overline{\overline{D}}_{g,\beta}$ is the dispersion coefficient [M^2·T^{-1}], $\lambda_{o-g,\beta}$ is the lumped mass transfer coefficient of β compound between NAPL and gas phase [T^{-1}] and $C_{g,\beta}$ and $C_{g,\beta}^{sat}$ are respectively the β compound concentration on the gas phase and the β compound concentration on the gas phase at saturation [M·L^{-3}].

Mass transfer limitations typically cause volatilization of NAPL in the subsurface to be a non-equilibrium process. The interface mass transfer can be approximated by Fick's first low (Weber and DiGino, 1996)). The masse transfer coefficient λ_f is deduced from the lumped mass transfer coefficient λ which is the product of the mass transfer coefficient and specific interfacial area per unit volume of reactor (Miller et al., 1990; Powers et al., 1992; Chao et al., 1998).

Rathfeled et al. (1991) described mass transfer at the NAPL/gas interface with kinetic model. They considered that the mass transfer is controlled by the diffusion rate on each side of the interface that and no resistance to transfer is encountered at the interface. The diffusion resistance on one side of the interface is often considered as dominant. It becomes, mass transfer rates can be described with a single overall mass transfer coefficient.

Several authors (Abriola et al., 1999; Rathfelder et al., 2000; Zhao, 2007) use a first-order rate expression for NAPL volatilization. The volatilization coefficient for a first-order rate expression is a function of several factors. The most difficulty in the process simulation at real scale is to found the mathematical relation which can estimate this coefficient based on the flow, porous media and pollutant characteristics and NAPL content. Hence, empirical models methods are generally used to estimate the lumped mass transfer coefficient. These models can be divided into two types: NAPL saturation independent models (Wilkins et al., 1995; Yoon et al., 2002) and NAPL saturation dependent models (Anwar et al., 2003; Harper et al., 2003). In other hand the most widely used models neglect the longitudinal dispersivity (Wilkins et al., 1995; Yoon et al., 2002).

The longitudinal dispersivity α_L with the molecular diffusion coefficient gives the dispersion coefficient in the mass conservation equation (equation [2]). It represents the mechanical dispersion due to the heterogeneity of the fluid flow velocity in the porous media. The dispersivity is an important pollutant transport property difficult to be measured experimentally. It can be estimated from the tracer breakthrough curves using analytical or numerical solution of the mass conservation equation.

$$\overline{\overline{D}}_{g,\beta} = \varepsilon\, D_{g,\beta}^o + \alpha_L U_g \qquad [2]$$

Where $\mathcal{E}$ a form factor [-], $D^{\circ}_{g,\beta}$ is the molecular diffusion coefficient of compound β in the gas phase [$L^2 \cdot T^{-1}$] and U_g is the pore gas velocity of the gas phase [$L \cdot T^{-1}$].
In this paper, the determination of the NAPL/gaz mass transfer coefficient from proposed model in literature is studied. The effect of the negligence of the longitudinal dispersivity by these models is also studied.

Methods

The Sherwood number represents the ratio of the convective mass transfer to the rate of diffusive mass transport. A modified Sherwood number for volatilization process has been used in the literature to characterize volatilization of entrapped NAPL in porous media (Equation [3]).

$$\log(Sh_{o-g,\beta}) = b_0 + b_1 \log(Pe_{g,\beta}) + b_2 \log(d_o) \qquad [3]$$

Where d_0 is the normalized mean grain size [L]. It is defined by $d_0 = d_{50}/d_m$, where d_{50} is the mean grain size of soil and $d_m = 0.05$ cm as defined by the Department of Agriculture (van der Ham and Brouwers 1998, Yoon *et al.*, 2002). b_0, b_1 and b_2 are parameters. The Peclet number $Pe_{g,\beta}$ and the Sherwood number $Sh_{o-g,\beta}$ of compound β in the gas phase are defined respectively by equation [4] and equation [5]. The Peclet number represents the ratio of the advective transport rate to the diffusive transport rate.

$$Pe_{g,\beta} = \frac{U_g\, d_{50}}{D^o_{g,\beta}} \qquad [4] \qquad\qquad Sh_{o-g,\beta} = \frac{\lambda_{o-g,\beta}\, d^2_{50}}{D^o_{g,\beta}} \qquad [5]$$

An analytical solution of the equation 1 was used by Wilkins et al. (1995) and Yoon et al. (2002) which gives the same results as equation [3]. These authors are neglected the hydrodynamic dispersion $\overline{\overline{D}}_{g,\beta}$ equation [6])

$$\lambda^*_{o-g,\beta} = -\frac{q_g}{L_c} ln(1 - \frac{C_{g,\beta}}{C^{sat}_{g,\beta}}) \qquad [6] \quad \text{with} \quad \lambda^*_{o-g,\beta} = \varphi S_g \lambda_{o-g,\beta} \qquad [7]$$

The normalized concentration can be calculated according to the equation [8] derived from equation [6].

$$\frac{C_{g,\beta}}{C^{sat}_{g,\beta}} = 1 - \exp(\frac{\lambda^*_{o-g,\beta}}{3600} * \frac{L_c}{q_g}) \qquad [8]$$

In their work, Wilkins et al. (1995) used a column and testing several soils and several pollutants at stationnary state. They proposed an empirical correlation from their experimental results (equation [9]).

$$Sh_{o-g,\beta} = 10^{-2.79} \ Pe_{g,\beta}^{0.62} \ d_o^{1.82} \ , \ 0.02 < Pe < 20 \qquad [9]$$

Equation [10] was derived from modified Sherwood number (equation [9]):

$$\lambda^*_{o-g,\beta} = 10^{-0,4221} \ D_{g,\beta}^{o \ 0.38} \ U_g^{\ 0.62} \ d_{50}^{0.44} \qquad [10]$$

Using the same experimental conditions, Yoon et al. (2002) proposed another empirical relationship to calculate the mass transfer coefficient (equation [11]).

$$\lambda^*_{o-g,\beta} = 10^{-0,5842} \ D_{g,\beta}^{o \ 0.32} \ U_g^{\ 0.68} \ d_{50}^{0.34} \qquad [11]$$

This equation is derived from modified Sherwood number (equation [12])

$$Sh_{o-g,\beta} = 10^{-2.77} \ Pe_{g,\beta}^{0.68} \ d_o^{1.68} \qquad [12]$$

Yoon *et al.* (2002) did not state clearly the *Pe* range in their experiments.
The empirical models of Wilkins et al. (1995) and Yoon et al. (2002) introduced a gas phase content in the estimation of the mass transfer coefficient and neglected the hydrodynamic dispersion. van der Ham and Brouwers (1998) developed the following relationship:

$$Sh_{o-g,\beta} = 10^{-3.3} \ Pe_{g,\beta}^{0.82} d_o^{1.82} \ , \qquad 5 < Pe < 60 \qquad [13]$$

$$\lambda^*_{o-g,\beta} = 10^{-0,662} \ D_{g,\beta}^{o \ 0.12} \ U_g^{\ 0.88} \ d_{50}^{0,7} \qquad [14]$$

After comparison of measurements to predictions, van der Ham and Brouwers (1998) found that equation [14] is more accurate for $2 < Pe < 60$. However they recommended the Wilkins et al. (1995) model for *Pe* values less than 2.
Equations [10], [11] and [14] show a relationship between the mass transfer coefficient, the interstitial pore velocity and the mean granular diameter of soil particles.
The analytical solution of the pollutant mass conservation equation is a classical method. This equation concerns gas phase and NAPL/gas phase transfers expressed in one dimension geometry (equation [1]). It is proposed by van Genuchten *et al.*, (1982) at stationary state (equation [15])

$$\lambda_{o-g,\beta} = \frac{1}{4\overline{\overline{D}}_g} \left[\left(U_g - \frac{2\overline{\overline{D}}_g}{L_c} \ln(1 - \frac{C_{g,\beta}}{C_{g,\beta}^{sat}}) \right)^2 - U_g^{\ 2} \right] \qquad [15]$$

In which L_c represents the column length [L].

$\lambda^*_{o-g,\beta}$ can be calculated from this expression and equation [7].

The relative error of different models can be calculated by equation [16] considering a reference values $\lambda^*_{o-g\_ref}$.

$$RE = \frac{\lambda^*_{o-g} - \lambda^*_{o-g\_ref}}{\lambda^*_{o-g\_ref}} * 100 \qquad [16]$$

Results

In order to study the effect of the hydrodynamic dispersion, results of $\lambda^*_{o-g,\beta}$ obtained by different authors are reproduced. These are the following models:
- empirical model of Wilkins et al. (1995) (equation [10])
- empirical model of Yoon et al. (2002) (equation [11])
- empirical model of van der Ham and Brouwers (1998) (equation [14])
- analytical solution proposed by van Genuchten et al. (1982) using several α_L values (equation 15).
The experimental conditions of each author is summarized in table1. Wilkins et al. (1995) and Yonn et al. (2002) used column is of 5 cm of diameter and 10 cm in length. They used several types of sand. Van der Ham and Brouwers (1998) used column of 5.1 cm of diameter and 1m length with two types of sand.

		Wilkins et al. (1995)	Van der Ham and Brouwers (1998)	Yoon et al. (2002)
Soils	d_{50} [cm]	0.024 to 0.120	0.264 and 0.625	0.020 to 0.107
	Uniformity Index C_u [-]	1.19 to 3.50	1.19 to 3.50	1.19 to 3.50
	Porosity φ [-]	1.19 to 3.50	0.241 to 0.436	0.154 to 0.327
	water saturation S_w [-]	0.082 to 0.160	0.241 to 0.436	0.154 to 0.327
	NAPL Saturation S_o [-]	0.04 to 0.091	0.038 to 0.094	0.054 to 0.119
NAPL		Styrene - Toluene Tetrachloroethylene	n tetradecane	Toluene
Pore gas velocity [cm.s⁻¹]		0.05 to 1.5	4.53 to 18.6	0.05 to 1.5
Pe		0.015 to 2	5.3 to 58.4	**-**

Table 1
Operating conditions

Condition to neglect dispersion coefficient in the mass transfer coefficient estimation

Figure 1 shows the results of mass transfer coefficient against pore's velocity using various models. The lumped mass transfer coefficient is calculated from model of Wilkins et al. (1995) and van der Ham and Brouwers (1998) and Yoon et al., (2002). Wilkins model gives the same result than analytical solution of dispersion convection with α_L =0 which is not the case of Yoon model. The van der Ham and Brouwers model gives linear result different from the experimental ones, except for pore's velocity near to 10 cm·s⁻¹. The van der Ham model gives lower values than

other models with the exception of high pore's velocity. While the values obtained by the Yoon model are higher whatever the pore's velocity.
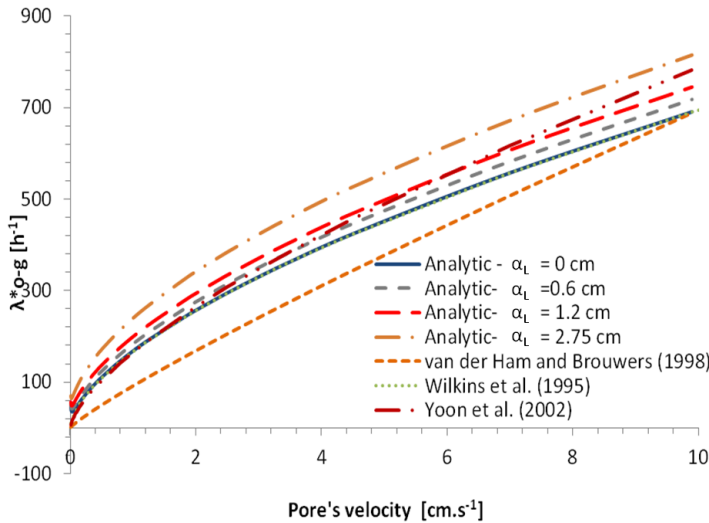

Figure 1
Mass transfer coefficient against pore's velocity simulated by various models

Figure 2 shows the results obtained of the normalized concentration against pore velocity. To identify results at low pore's velocity, logarithmic scale was used (figure 2 and figure 3).
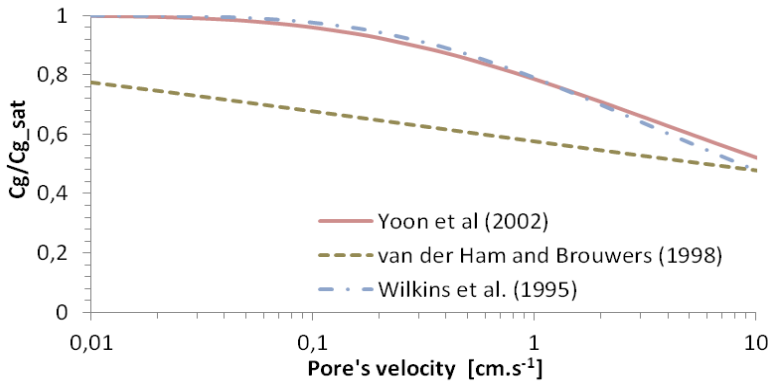

Figure 2
Normalized concentration against pore's velocity simulated by various models.

The empirical models show the validity of the local equilibrium in the case of a low pore velocity less than 0.1 cm·s^{-1} (*Pe*=0.084). In fact, the concentration at outlet is near to the concentration at saturation for lower pore's velocities and then decreases for Yoon and Wilkins model. These models give similar results. However the van der Ham model gives different values at low pore's velocities, this is in agreement with van der Ham and Brouwers (1998) conclusions whose found that equation [14] gives better results for 2 < *Pe* < 60. The model of Yoon et

al. (2002) gives a low estimation of concentration in the case of low pore velocity, and more important estimation in the case of high pore velocity compared to Wilkins et al. (1995) model. However, the difference between models is still modest; less than 15%. The lumped mass transfer coefficient found in the case of empirical models increases linearly for pore velocities ranging from 0.01 to 0.05 m·s^{-1}, while another behavior is observed with analytical solution of the convection-dispersion equation.
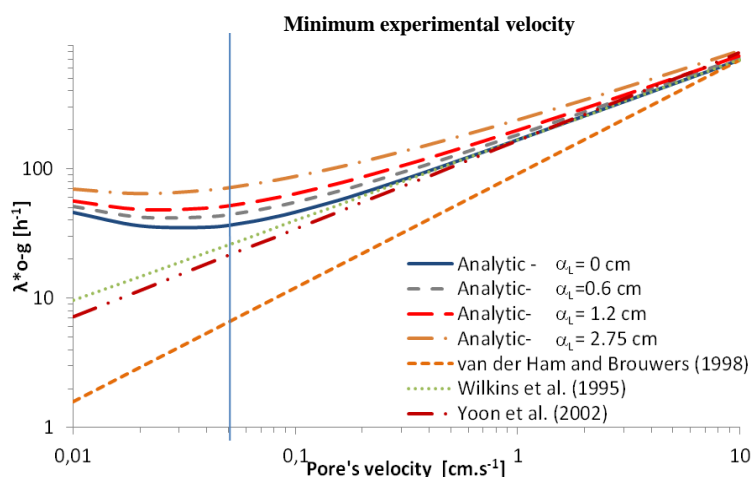

Figure 3
Comparison between NAPL/gas lumped transfer coefficient estimation model at low pore's velocity

Figure 4 shows the relative error of different models calculated by equation 16. Results given by Wilkins et al (1995) were considered as a reference values because of the quantity of experimental results for different conditions.
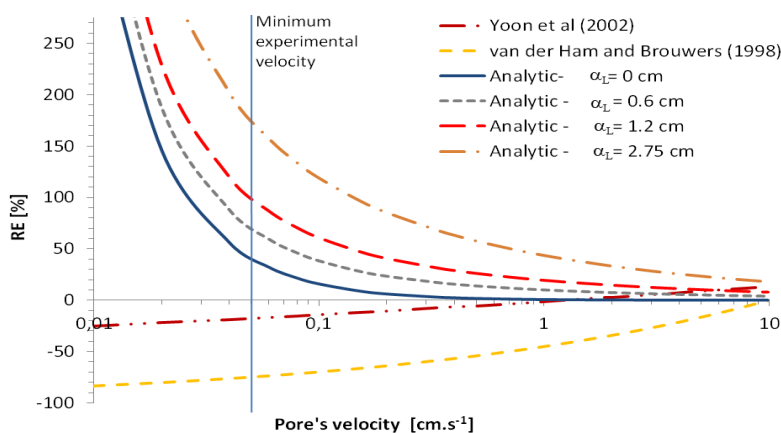

Figure 4
Relative comparison between NAPL/ gas mass transfer estimation models

The effect of the negligence of the dispersion coefficient is observed for pore velocities less than 0.3 cm·s^{-1} (*Pe*=0.25), where relative error is more than 40% for α_L=1.2 cm. This effect is decreased in the case of more important pore velocities.

Although the dispersion coefficient is neglected, the molecular diffusion has an important role in the case of lower velocities, where error is more than 30% for velocities less than 0.06 cm·s^{-1} (*Pe*=0.05). The models of Wilkins *et al.,* (1995) and Yoon *et al.,* (2002) are then experimentally validated in the case of pore velocities superior to 0.3 cm·s^{-1} (*Pe*=0.25). Indeed some authors define an influence radius of extraction well of SVE at an area where pore velocity exceeds 0.01 cm·s^{-1} (DiGiulio et al., 2001; Dixon et al., 2006 ; U.S. ACE, 2002). Then a correction of these models is need for low velocities, where effect of hydrodynamic dispersion is important.

Conclusion

Models for determination of NAPL/gas mass transfer coefficient from literature are tested to evaluate the influence of the negligence of the dispersion coefficient by these models. It has been shown that hydrodynamic dispersion cannot be neglected in estimating the mass transfer coefficient for all gas velocities. This result is very important because it shows that the use of these models requires a correction especially for low pore's velocities.

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EFFECT DU COEFFICIENT DE DISPERSION SUR LA DETERMINATION DU COEFFICIENT DE TRANSFERT DE MASSE PLNA/GAZ
Resumé

Les polluants organiques sont les polluants les plus répondus dans les sols. Afin d'évaluer la propagation du polluant et d'appliquer une technique de remédiation, il est nécessaire de connaitre les paramètres de transfert entre le polluant et les composants du sol. L'évaporation de la Phase Liquide Non Aqueuse « PLNA » est le phénomène le plus étudié principalement lorsque la technique d'Extraction sous pression de vapeur est utilisée. Le coefficient de transfert de masse PLNA/gaz est le paramètre qui décrit cette évaporation. Plusieurs relations sont définies pour déterminer ce coefficient en négligeant le coefficient de dispersion. Des modèles empirique de la littérature pour la détermination du coefficient local de transfert de masse PLNA/gaz "λ" sont utilisés dans ce travail. Les résultats sont comparés aux résultats de la solution analytique de l'équation de convection dispersion. L'influence de la dispersivité longitudinale α_L dans la détermination de λ est évaluée. Ila été démontré que le coefficient de dispersion peut être négligé dans les modèles de détermination de λ pour des vitesses de pores supérieur à 0.1 cm.s^{-1}. Une correction est nécessaire pour les faibles vitesses de pore.

Mots clés: *milieu poreux, coefficient de transfert PLNA/gaz, dispersivité longitudinale*