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Highlighting of a local Non-Equilibrium Thermodynamics during the transfer of trichloroethylene (TCE) in the superficial layers of Arid Soils.

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Abstract

In this paper, we analyze and model the mass transfer of trichloroethylene in the surface layer of a soil. Our study essentially focuses on arid soils taking into account the phase change liquid-vapor. We have then examined the validity of the assumption of local equilibrium by comparing the values of the instantaneous pressure of the trichloroethylene vapor and the equilibrium vapor pressure during the transfer process. It appears that the assumption of local equilibrium during the transfer of trichloroethylene cannot be admitted.

Keywords: transfer; non-equilibrium; trichloroethylene; arid soil; phase change.

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Nomenclature

C_T	TCE concentration in aqueous phase	(kg.m ⁻³)
C_{T0}	TCE initial concentration in aqueous phase	(kg.m ⁻³)
D_T^a	Diffusion coefficient of TCE vapor in air	(m ² s ⁻¹)
D_T^w	Diffusion coefficient of TCE in water	(m ² s ⁻¹)
D_w^a	Diffusion coefficient of water vapor in air	(m ² s ⁻¹)
g	Acceleration of gravity	(m ² /s)
J_T	Evaporation flux of TCE	(kg m ⁻² s ⁻¹)
J_w	Evaporation flux of water	(kg m ⁻² s ⁻¹)
K_{ns}	Permeability of liquid phase in soil	(m/s)
K_{sat}	Saturation permeability of liquid in soil	(m/s)
L_H	Evaporation coefficient of heptane	(kg K s m ⁻⁵)
L_T	Evaporation coefficient of TCE	(kg K s m ⁻⁵)
L_w	Evaporation coefficient of water	(kg K s m ⁻⁵)
M_H	Molar weight of heptane	(kg mol ⁻¹)
M_T	Molar weight of TCE	(kg mol ⁻¹)
M_w	Molar weight of water	(kg mol ⁻¹)
P_H^{eq}	Equilibrium vapor pressure of heptane	(Pa)
P_H^v	Vapor pressure of heptane	(Pa)
P_T^{eq}	Equilibrium vapor pressure of TCE	(Pa)
P_T^v	Vapor pressure of TCE	(Pa)
P_w^v	Vapor pressure of water	(Pa)
P_w^{eq}	Equilibrium vapor pressure of water	(Pa)
R	Ideal gas constant	(J K ⁻¹ mol ⁻¹)
v_L	Barycentric velocity of liquid phase	(m/s)
w_L	Liquid content	(%)
w_L^r	Residual liquid content	(%)
w_L^{sat}	Saturation liquid content	(%)
w_{L0}	Initial liquid content	(%)
w_0	Initial water content	(%)
ϕ_g	Volume fraction of gas	(%)
ρ_T^v	Apparent mass density of TCE vapor	(kg m ⁻³)
ρ_w^L	Apparent mass density of water liquid	(kg m ⁻³)
ρ_w^v	Apparent mass density of water vapor	(kg m ⁻³)
ρ_T^L	Apparent mass density of aqueous phase of TCE	(kg m ⁻³)

1. Introduction

The description of a pollutant transfer as trichloroethylene in the surface layers of a dry soil deserves the attention of the scientific community regarding the resolution of problems related to environmental sciences (Braidia & Ong, 2000). However, understanding the phenomena involved in the transfer of a compound in a soil is very difficult because many phenomena are coupled during transfer processes in a multiphase medium which can deform, and where the fluid contents can vary in time and space. Accordingly, any modeling used to describe and predict the dynamic behavior of a volatile compound in an arid soil must be preceded by an experimental investigation to determine the essential parameters involved in the phenomena (Auriault & Lewandowska, 1997). Most bibliographic works use a classical approach to describe mass transfer in soils, assuming that the continuous phase of the porous medium fully and instantaneously participates to the mass transfer (Dridi & Schäfer, 2006). Such transfer process occurs in the saturated zone of the soil and can be well described by the Darcy's law. In these conditions, it is considered that water is not entirely adsorbed by the solid particles; so that the liquid/vapor equilibrium described by Henry's Law ($P_T^{eq} = K_H C_T$) can be applied. However, several studies in the literature showed that the low water contents are responsible of soil hygroscopic effects causing a deviation of the water activity. Recent studies realized on water showed that these effects can modify not only the equilibrium between phases but the kinetics of phase change (Chammari et al., 2003; Ouedraogo et al., 2013). It is therefore logical to wonder if in such circumstances the conventional assumption of equilibrium can still be applied. Otherwise, it becomes necessary to find the suitable way to describe the liquid-vapor phase change dynamics; that is the objective of the present article.

2. Materials and Method

2.1. Presentation of the System and Definition of Initial Conditions

The system studied in this work is a portion of soil containing a liquid phase (subscript L) composed of water (denoted by w) and dissolved TCE (denoted by T) and a gas phase (denoted by g) composed of air (denoted by a). The physic-chemical properties of TCE and the soil sample are respectively given in Tables 1 and 2.

Table 1. TCE physic-chemical properties at 30 °C.

Equilibrium vapor pressure /Pa	Henry's constant /Pa m ³ mol ⁻¹	Solubility /Mg litre ⁻¹
11912	1195.5	1310

Table 2. Main characteristics of the soil.

Particle size 0-2 mm	Particle density 2650 kg. ⁻³	Apparent mass density 1500 kg. ⁻³	Porosity 43%
quartz content 40%	calcite content 45-50%	clay content 10%	
organic matter 0.28%	organic carbon 0.16%	total N 0.10%	C/N 16.83
w_L^{sat} 28.9%	w_L^r 1%	K_{sat} 3.10^{-5} m.s ⁻¹	

Considering the experimental conditions the following assumptions are admitted (Ouoba et al., 2014a):

- A1: the solid phase is chemically inert and incompressible,
- A2: the temperature is uniform and constant,
- A3: the gas behaves as an ideal gas mixture and is assumed to be stationary so that the filtration flux of the gaseous phase is zero,
- A4: the liquid phase is an ideal dilute solution of water and TCE,
- A5: there are no chemical reactions in liquid and gas phase. The only physic-chemical phenomenon taken into account is the liquid-gas phase change of water and TCE,
- A6: the pressure of the gas is uniform, constant and equals to atmospheric pressure,

The previous validation procedures proved the reliability of the theoretical model in the case of pure water; particularly the phase change phenomenon is accurately described by the model (Bénet et al., 2009; Lozano et al., 2008; Ouedraogo et al., 2013). Thus, in this section, dissolved TCE is considered to study the non-equilibrium between the phases. The phenomenological evaporation coefficient has not been experimentally determined for dissolved TCE. That is the reason why as a first approximation, we adopted for the evaporation coefficient of dissolved TCE the same expression than that obtained for pure TCE.

The conditions on water are:

- The initial water content of soil is uniform;
- The relative humidity of air in the chamber is set to 30% or to 50%.

The tests of simulation have been performed on soil columns with 30 cm of height and 7.5 cm of diameter, where the liquid phase is a solution of TCE with a known initial concentration. The problem is considered as one-dimensional so that the initial conditions are defined by:

- $w_L(t = 0, z) = w_{L0}$
- $P_w^v(t = 0, z) = P_w^{veq}(w_{L0})$
- $C_T(t = 0, z) = C_{T0}$
- $P_T^v(t = 0, z) = P_T^{veq}(C_{T0})$

2.2. Basic equations of transfer

A classic approach of mass balance in a Representative Elementary Volume (REV) provides the equations of transfer of water and TCE in the aqueous phase. We then obtain:

For liquid water

$$\frac{\partial \rho_w^L}{\partial t} + \underbrace{\nabla(\rho_w^L v_L)}_{\text{term of filtration}} = \underbrace{-J_w}_{\text{phase change}} \quad (1)$$

For the vapor of water

$$\frac{\partial \rho_w^v}{\partial t} - \underbrace{\nabla(D_w^a \nabla \rho_w^v)}_{\text{term of diffusion}} = \underbrace{J_w}_{\text{phase change}} \quad (2)$$

Where the diffusion coefficient of water vapor in air, given by Ouedraogo et al. (2013) is:

$$D_w^a = 2,57 \times 10^{-5} m^2/s.$$

For the aqueous phase of TCE

$$\frac{\partial \rho_T^L}{\partial t} + \underbrace{\nabla(\rho_T^L v_L)}_{\text{term of filtration}} - \underbrace{\nabla(D_T^w \nabla \rho_T^L)}_{\text{term of diffusion}} = \underbrace{-J_T}_{\text{phase change}} \quad (3)$$

Where the diffusion coefficient of TCE in water, given by Mahmoodlu et al. (2014) is:

$$D_T^w = 9,1 \times 10^{-6} m^2/s.$$

For the vapor of TCE

$$\frac{\partial \rho_T^v}{\partial t} - \underbrace{\nabla(D_T^a \nabla \rho_T^v)}_{\text{term of diffusion}} = \underbrace{J_T}_{\text{phase change}} \quad (4)$$

Where the diffusion coefficient of TCE in air, given by Mahmoodlu et al. (2014) is:

$$D_T^a = 7,9 \times 10^{-6} m^2/s.$$

The term of filtration of the liquid phase is given by:

$$\rho_w^L v_L = -\frac{K_{ns}}{g} (\nabla P_w^L + \rho_w^L g) \quad (5)$$

Where the coefficient of permeability of soil is given by Ouedraogo et al. (2013)

$$K_{ns}(w_L) = K_{sat} \left(\frac{w_L - w_L^r}{w_L^{sat} - w_L^r} \right)^\lambda \quad (6)$$

In this relation the coefficient $\lambda=5$

It is important to note that for each compound, the transfers within the two phases are coupled by phase change phenomena through the evaporation rates, J_w and J_T given by Bénet et al. (2009):

$$J_c = L_c \frac{R}{\phi_g M_c} \ln \left(\frac{P_c^v}{P_c^{veq}} \right), \quad c = T, w \quad (7)$$

Where P_c^{veq} is given by Ouoba et al. (2010a).

The coefficient of phase change given by Equation (7) has been successfully used by Ouoba et al. (2015) in recent publications. Its determination necessarily requires an experimental study and allows determining the evaporation kinetics. It depends on the state variables (temperature T , liquid content w_L), soil properties (composition, texture, compactness, etc.), but no explicit expression is available (Lozano et al., 2008; Ruiz & Benet, 2001).

2.3. Experimental Device and Principle

The experimental device used to determine the phase change coefficient of a pure liquid in a porous medium is depicted in **Figure 1**. It was initially developed to measure water activity and has been called “activity-meter”. This device and the associated method were validated in our previous works (Ouoba et al., 2014b; Ouoba et al., 2010a) and have been patented in Europe and United States (Bénet et al., 2012). The sample (a) is placed against a pressure transducer (b) (Druck, PMP4030AB) and a temperature thermocouple (c) (type K). This records the total pressure of the gas, P_g , and its temperature, T , throughout the test. Data acquisition is performed through a National Instrument DAQ card and analyzed using LabView. A piston pump (d) is placed above the sample to impose a gas pressure below atmospheric pressure. The piston chamber volume is controlled by a screw system (e) with a graduated ruler (f). O-ring gaskets ensure perfect air tightness so that the system can be considered thermodynamically closed. The dimensional characteristics of the device are given by Ouoba et al. (2010b). The whole device is placed in a thermo-regulated bath to ensure a constant temperature. Because the device is made of stainless steel, its high thermal inertia leads to weak temperature variations and thermal equilibrium is experimentally observed.

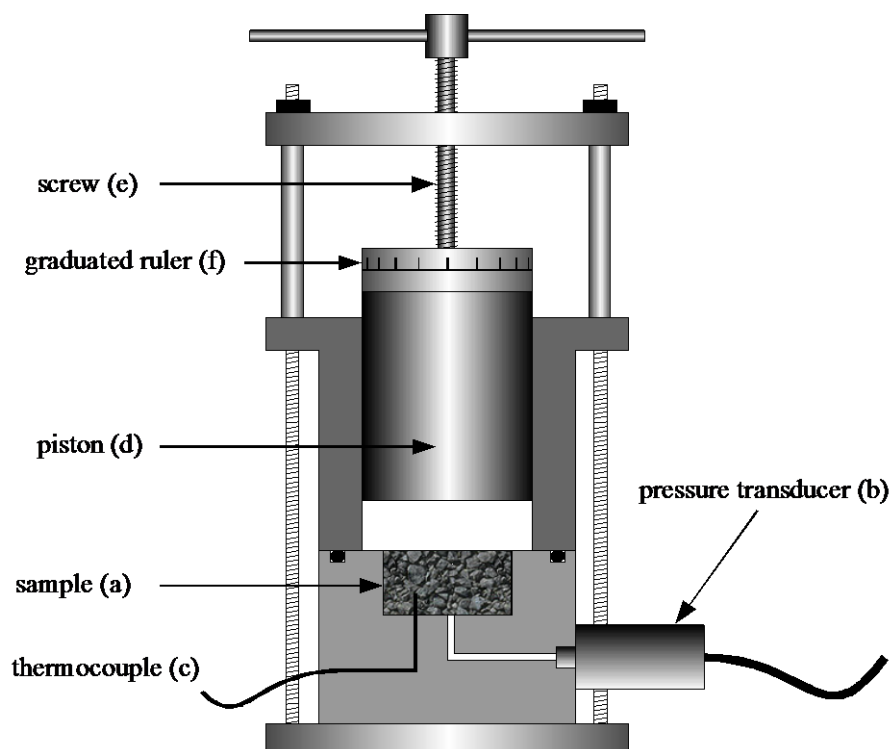


Figure 1. Schematic diagram of the activity-meter.

3. Results and Discussion

3.1. Determination of the evaporation coefficient of TCE

To describe the hygroscopic effects in the transfer process of a compound in an arid soil, it is necessary to consider the liquid/vapor phase change associated with the transfer of this compound. The method used to determine the evaporation coefficient of TCE is largely developed in Ouoba et al. (2014a). It is based on the principle used by Naon et al. (2013) for heptane and by Ouedraogo et al. (2013) for water. We compare in **Figure 2** the evaporation coefficients of water, heptane and TCE. One can see that the evaporation coefficient of water is lower than that of heptane and TCE. The evaporation coefficient of TCE is about 7 times higher than that of heptane. These results are related to the highest volatility of TCE compared to the one of heptane and water. Indeed, it is well known that the higher the volatility of a compound, the greater its saturated vapor pressure. According to literature data (Ouoba et al., 2010b), at the same temperature $P_w^{eq} < P_H^{eq} < P_T^{eq}$ which what is in agreement with the results of **Figure 2**.

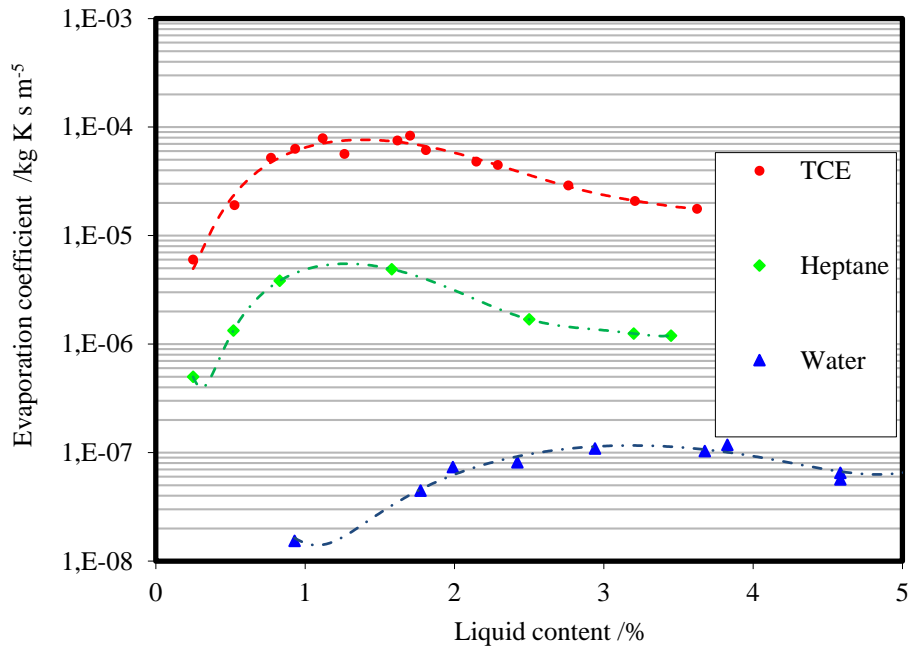


Figure 2. Evaporation coefficients of water, heptane and TCE at 30 °C.

3.2. Validation of the numerical model

The validation of the numerical model has concerned water. The transfer equations established for water are discretized by using the following approach:

- An implicit scheme in time;
- An upstream biased for the convection flow diagram;
- Considering the non-linearity of the transfer equations, we chose the Newton-Raphson's method for the numerical solution of the problem.

To validate the numerical model, a comparison has been made between numerical results and experimental results.

The experiments consisted in making soil columns with initial liquid content w_L compacted in PVC (**Figure 3**). These soil columns were placed in a climatic chamber where temperature and relative humidity were controlled. The columns were let to evolve in the climatic chamber for various experimental drying times. The samples were then removed from the chamber and sliced in order to determine the water content profiles corresponding to a given drying time.

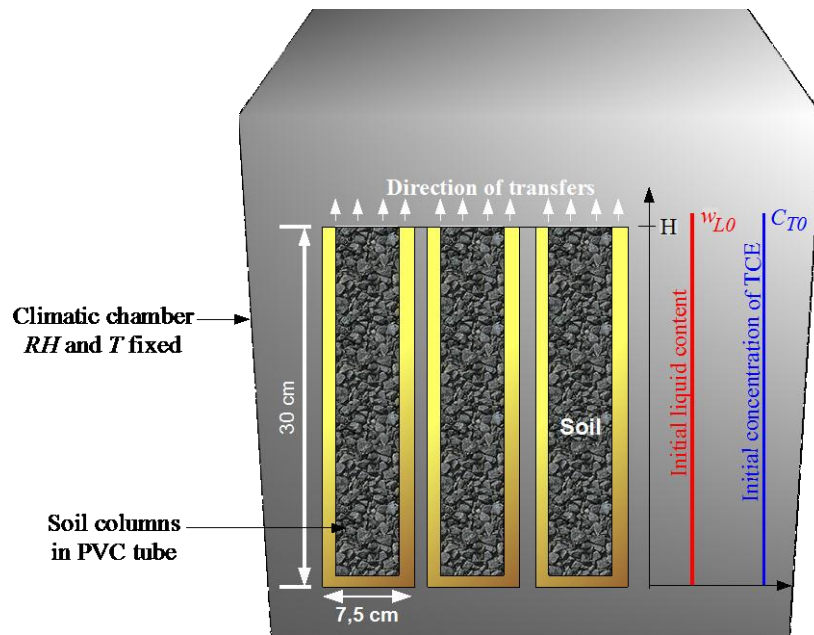


Figure 3. Climate chamber containing soil samples.

The experimental and numerical drying kinetics for two values of the relative humidity, namely $RH=30\%$ and $RH=50\%$, are presented in **Figure 4**. This figure represents the average water content of the sample as a function of time. We can notice that there is a good agreement between experimental and simulated curves.

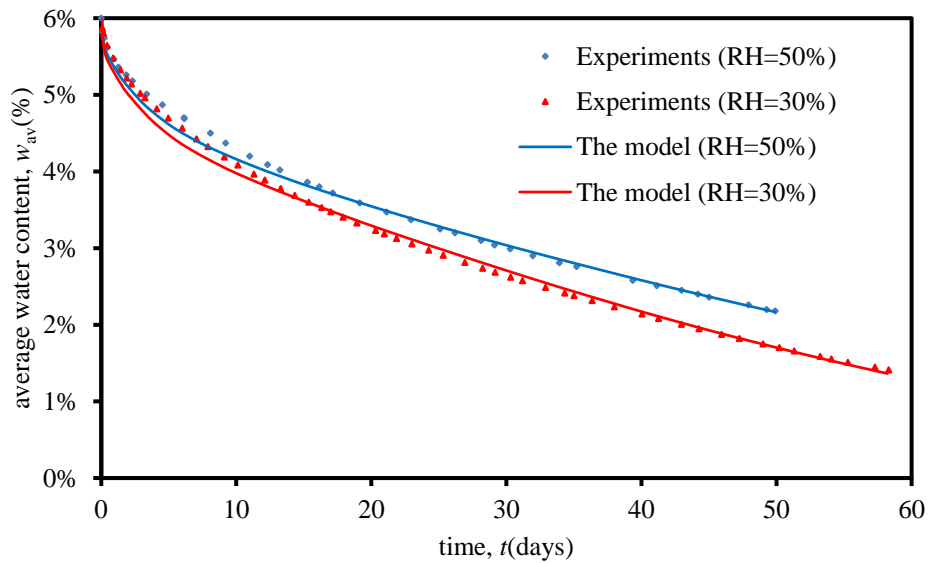


Figure 4. Kinetics of drying for an initial water content $w_0 = 6\%$ and for two values of relative humidity $RH=50\%$ and $RH=30\%$.

Figure 5 presents the experimental and simulated water content profiles. It may also be noted in this figure that there is a good agreement between both profiles. The differences in the vicinity of the surface may be partly due to possible imperfections of the model but also to errors of measurement during the extraction of the sample and its destruction for measurement.

The profiles highlight a rapid drying front at the beginning of the experience, but much more important near the surface. The examination of the numerical results also shows a significant decrease in water content in the vicinity of the surface a few hours after the starting of the experiment. This value of water content reaches immediately the equilibrium moisture content (0.24 %) and remains constant as shown by all the curves that admit a common point

at the surface. At the beginning of drying, the water content in the lower part of the column increases above the initial water content due to gravitational drainage. This phenomenon is accurately predicted by the theoretical model. As the numerical results are in good agreement with experiments for water, the model has been used to describe the transfer of dissolved TCE using the evaporation coefficient of pure TCE.

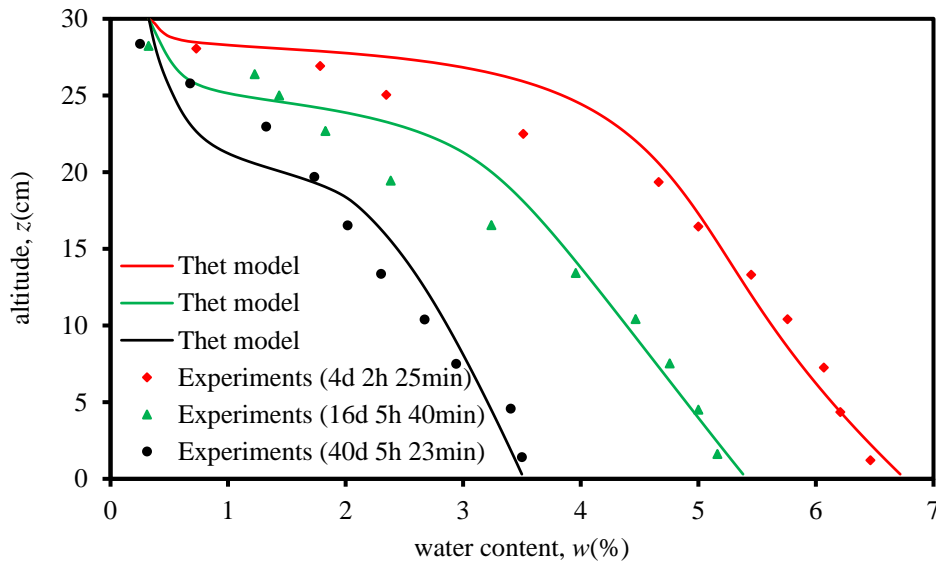


Figure 5. Profiles of water content for $RH=30\%$.

3.3. Highlighting of a thermodynamic non-equilibrium between liquid and vapor phases

The curves of **Figure 6** present an instantaneous vapor pressure profile of TCE, P_T^v , and the corresponding equilibrium vapor pressure profile, P_T^{veq} . The two curves are significantly different which means there is not equilibrium between the dissolved TCE and its vapor.

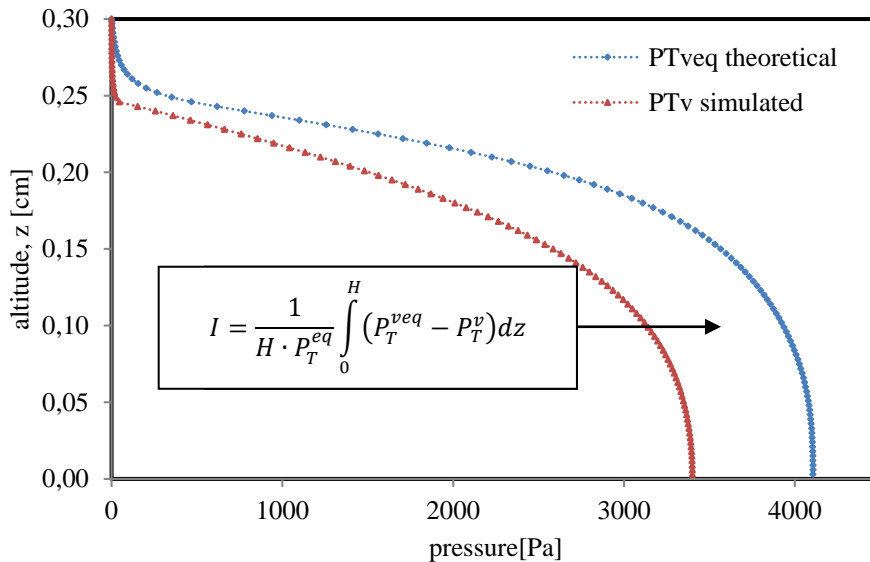


Figure 6. Values of the pressures P_T^v [Pa] and P_T^{eq} [Pa] for a time $t=500,000$ s for $w_0=3\%$ and $C_{T0}=1000$ g/L.

Similar results have been found for other simulation times. Hence, the only parameter that may be responsible of this disequilibrium is the coefficient of phase change. To investigate the influence of the evaporation coefficient of dissolved TCE on the disequilibrium and to better understand the conditions under which the assumption of local

equilibrium could be admitted, simulations were performed multiplying the evaporation coefficient of pure TCE by a factor α ranging from 10^{-4} to 10^2 . The parameter chosen to quantify the disequilibrium is:

$$I = \frac{1}{H \cdot P_T^{veq}} \int_0^H (P_T^{veq} - P_T^v) dz \quad (18)$$

This integral is a dimensionless representation of the area between the curves P_T^v and P_T^{veq} (Figure 6). So, Figures 7 and 8 represent the variation of I as a function of α for different values of water contents. Figure 7 corresponds to a relative humidity of 30% and for an initial concentration $C_{T0} = 100$ mg/L and Figure 8 is obtained for a relative humidity of 50% and for an initial concentration $C_{T0} = 1$ mg/L.

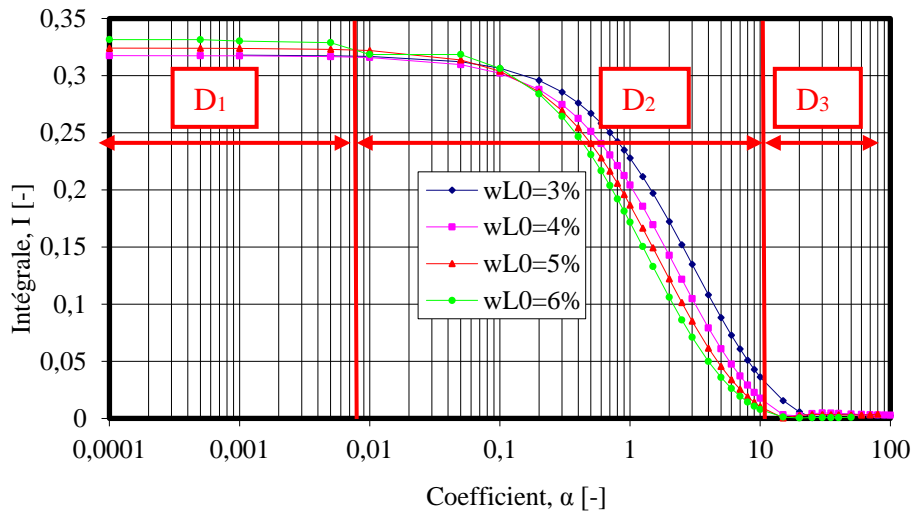


Figure 7. I value as a function of α for $RH=30\%$ and $C_{T0}=100$ mg/L.

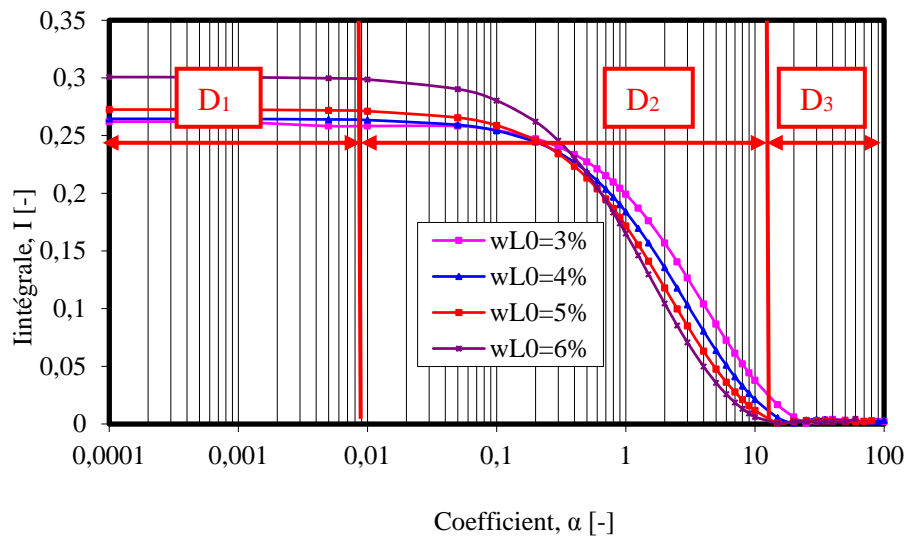


Figure 8. I value as a function of α for $RH=50\%$ and $C_{T0}=1$ mg/L.

Both Figures highlight the existence of three domains:

- A first domain called D_1 in the interval $10^{-4} \leq \alpha \leq 10^{-2}$ where the dimensionless integral I has a value substantially equal to 0.325. Within this interval it is not possible to apply the local equilibrium assumption.

Because of the low value of the evaporation coefficient, the transfers are mainly due to capillary actions and surface evaporation,

- A second domain designated by D_2 in the interval $10^{-2} \leq \alpha \leq 13$ where $0,325 \leq I < 0$. The disequilibrium decreases but the assumption of the local equilibrium is still not applicable. The mechanisms of phase change are fairly low and all the transfer phenomena are competing,
- A third domain D_3 for $\alpha > 13$ where the value of the dimensionless integral I is almost zero. In this interval, the values of P_T^v and P_T^{veq} are the same and the instantaneous equilibrium is reached.

These results have shown that the local equilibrium cannot be admitted in the modeling of TCE transfer in an arid soil. It is unlikely that the evaporation coefficient of dissolved TCE would be 13 times higher than that of pure TCE. It is rather likely that, for dissolved TCE, coefficient α is lower than 1.

4. Conclusion

In this study, the kinetics of phase change has been characterized for water, heptane and TCE confirming other studies realized on water, i.e., the return to equilibrium is not instantaneous. We have shown that the non-equilibrium is due to the phase change kinetics and we experimentally determined the evaporation coefficient of water, TCE and heptane. From these experiments, explicit expressions of these characteristics have been identified and introduced in a numerical model. The results for water obtained on soil columns with 30 cm of height and 7.5 cm of diameter were compared with the results of the model. This confrontation between the experiments and the model has shown that the proposed model can be used to describe the transfer of water in the soil taking into account the phase change. As the numerical results are in good agreement with experiments for water, the model has been used to describe the transfer of TCE in the aqueous phase of soil. The numerical results have shown that during transfer of TCE in the aqueous phase, there is a substantial difference between the actual vapor pressure of TCE, P_T^v , and the equilibrium vapor pressure, P_T^{veq} , so the assumption of local equilibrium commonly accepted in the literature is not admitted here for TCE. However, awaiting for other researches in other experimental conditions, the results presented in the present work are only valid when the transport of TCE is performed under the same conditions with the same assumptions as these admitted in this work.

The contribution of this work has enabled to highlight the importance of phase change on transport of volatile organic compound in hygroscopic soil. However, additional studies need to be extended to other types of soils with different physic-chemical characteristics in order to confirm the results of this work. It would also be desirable to undertake a large-scale study on soil columns and in situ by taking into account more experimental variables such as coupling phenomena and variation of porosity in the medium that can help to improve the numerical model. Finally, it would be important to include in the numerical model most of the mechanisms involved in the transport processes such as chemical reactions, photo-degradation...

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