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Evaporation of a volatile organic compound in a hygroscopic soil – influence of the airflow and its VOC vapour saturation

Bétaboalé Naon*- Jean-Claude Bénéte***, Bruno Cousin**, Fabien Cherblanc**, Ali Chammari **

* *Université Polytechnique de Bobo-Dioulasso, 01 B.P. 1091, Bobo-Dioulasso, Burkina-Faso.*

** *Laboratoire de Mécanique et Génie Civil, Université Montpellier 2, CNRS, cc 048, Place Eugène Bataillon, 34095 Montpellier, cedex 5, France.*

jean-claude.benet@univ-montp2.fr

ABSTRACT. This article presents an experimental and theoretical study of VOC volatilization in soil during a decontamination process by vapour extraction or venting. A phase change law is proposed in the case of a sandy-silty soil when the convective gaseous phase is vapour-charged. A simple experimental method for analyzing the phase change is presented. Finally, an efficiency coefficient is introduced to quantify the contribution of airflow velocity on venting.

RESUMÉ. Cet article présente une étude expérimentale et théorique de la volatilisation d'un COV dans un sol soumis à une décontamination par ventilation. On propose une relation de changement de phase dans le cas convectif pour un limon sableux hygroscopique lorsque l'air en mouvement est chargé de vapeur de COV. Une méthode expérimentale simple d'analyse du changement de phase est proposée. Finalement un coefficient d'efficacité est introduit pour quantifier l'influence de la vitesse de l'air sur l'efficacité de la ventilation.

KEYWORDS: venting, phase change, mass transfer, modelling, natural attenuation.

MOTS-CLÉS: dépollution par ventilation, changement de phase, modélisation, atténuation naturelle.

Introduction

Phase change processes play a predominant role in decontamination operations for soils contaminated by volatile organic compounds (VOC):

- evaporation of the pollutant in non aqueous phase liquid (NAPL) or adsorbed on the solid phase,
- volatilization of the dissolved aqueous phase pollutant,
- direct dissolution in water of the pollutant in NAPL or adsorbed on the solid phase.

Mass transfer phenomena between phases are not instantaneous and modelling should account for phase change kinetics, even if this is seldom the case in the available models (Mulligan and Yong, 2004; Zhao and Zytner, 2005). This is particularly true in the decontamination process by vapour extraction or venting. Several experimental studies have shown non-equilibrium between the gas phase and the other phases of the soil (Lingineni and Dhir, 1997, Wilkins *et al.*, 1995, Yoon *et al.*, 2002). On-site observations also confirm the non-equilibrium between the different phases. For instance, high extraction rates are generally obtained during the first days of treatment. Extracted vapour concentration is then seen to drop, signifying a state of non-equilibrium between the different phases of the soil. Decontamination objectives generally requires continuing treatment for several months or even years, at low extraction rates (Zhao and Zytner, 2008). It is often reported that in the tailing phase, high recovery rates can be achieved for a short period after interrupting pumping (Wilkins *et al.*, 1995). However, some simulations (Armstrong *et al.*, 1994) show that intermittent treatment appears to be less effective than continuous pumping at the same average rate in the case of a dissolved aqueous phase VOC. Several authors (Poulsen *et al.*, 1996; Rathfelder *et al.*, 2000) stress the marked influence of NAPL phase – gas phase change kinetics on decontamination. Yet few studies have been devoted to this phase change as underlined by Yoon *et al.* (2002).

Soils are generally hygroscopic: at thermodynamic equilibrium, the partial pressure of the vapour of a liquid constituent in the soil is lower than the equilibrium pressure of the same constituent in a pure liquid phase, in the free state, at the same temperature. This is due to the presence of particles of clay or organic matter produced by plant, animal and human activity. Hygroscopicity increases the binding energy between VOC and solid phase and affects the rate of phase change (Bénet *et al.*, 2009).

Among the various processes involved, one of the most sensitive is focused on in this study: NAPL/adsorbed phase/gas phase change in the hygroscopic domain. The phase change of a liquid VOC contained in a soil will be examined in two very distinct cases:

- the case where the gas phase is immobile. In this case, diffusive mass transport is predominant in the gas phase. It will be referred as the “diffusive case”,

- the case where the gas phase is mobile, which occurs during a venting operation. Henceforth, this case will be called the “convective case”.

The main objective of this article is to propose a phase change law in the convective case for a hygroscopic soil taking account of VOC vapour saturation of the air. A simple experimental method to determine the phase change coefficient in this case is also presented. Finally, the efficacy of venting is analysed with respect to the diffusive case, which corresponds to an immobile gas phase.

This study comes within the framework of the following hypothesis:

- the solid phase constituted by particles of soil is chemically inert and its deformations are not considered,
- temperature is uniform and constant,
- the liquid phase is constituted by a single-species volatile NAPL and does not flow,
- biodegradation will not be considered,
- the gas phase of the soil is composed of air, considered as a single constituent, and VOC vapour.

The experimental protocols were designed to comply with these assumptions.

2. Mathematical Modelling

The theoretical model of decontamination by venting of a soil contaminated by a NAPL presented hereafter directly derives from models of mass transfer in multi-phase media (Prigogine and Mazur, 1951, Truesdell, 1960; Bénét and Jouanna, 1983, De Groot and Mazur, 1984; Müller, 2001). This model constitutes the theoretical framework of our study and defines the variables used. The model applies to both convective and diffusive transport. Only the expression of the phase change term will depend on the case under consideration.

2.1. Mass balance equations

Mass balances are developed using the bulk densities of the NAPL phase, ρ_l , the VOC constituent in the gas phase, ρ_v , and the air constituent in the gas phase, ρ_a . The bulk density is defined as the ratio of the phase or constituent mass divided par the total unit volume [$\text{kg}\cdot\text{m}^{-3}$]. Real densities are linked to the bulk densities by the relation:

$$\rho_i = n_g \rho_i^* \quad i = a, v \quad [1]$$

where the gas phase volume fraction n_g [] is defined as the ratio of gas phase volume to the total volume.

The ideal gas law relates the bulk densities ρ_v and ρ_a to the vapour partial pressures of VOC p_v and air p_a [Pa]:

$$\rho_i = \frac{n_g M_i}{R T} p_i \quad i = a, v \quad [2]$$

where M_i [kg.mol⁻¹] is the molar mass, R [J.mol⁻¹.K⁻¹] the ideal gas constant, T [K] the temperature.

The liquid and gas VOC contents are defined as:

$$w_l = \frac{\rho_l}{\rho_s} \quad [3]$$

$$w_v = \frac{\rho_v}{\rho_s} \quad [4]$$

Regarding the VOC in gas or NAPL phases, its molar mass is identical in both. To simplify, it will be written M in the following development. According to [2], the VOC content can be written:

$$w_v = \frac{n_g M}{R T \rho_s} p_v \quad [5]$$

Thus, the total VOC content is given by:

$$w = w_l + w_v = w_l + \frac{n_g M}{R T \rho_s} p_v \quad [6]$$

The state variables chosen to describe the system are the total VOC content w and the VOC vapour partial pressure p_v . Assuming the liquid phase is immobile, the mass balance equation of VOC in the liquid phase is given by:

$$\rho_s \frac{\partial w_l}{\partial t} = -\hat{\rho}_v \quad [7]$$

where $\hat{\rho}_v$ [kg.m⁻³.s⁻¹] is the rate of VOC evaporation per unit volume. In the gas phase, the mass balance equation can be written:

$$\rho_s \frac{\partial w_v}{\partial t} + \nabla \cdot (\rho_v \mathbf{v}_g) = -\nabla \cdot \mathbf{J}_v + \hat{\rho}_v \quad [8]$$

where \mathbf{v}_g [m.s⁻¹] is gas phase velocity, \mathbf{J}_v [kg.m⁻².s⁻¹] is the vapour diffusion flux of VOC.

2.2. Phase change modelling

From a thermodynamic point of view, phase change is an irreversible phenomenon. The production of entropy σ [W.m⁻³] associated with this phenomenon is expressed as (Prigogine and Mazur, 1951; Müller, 2001; Bénet *et al.*, 2009):

$$\sigma = \hat{\rho}_v \frac{\mu_l - \mu_v}{T} \geq 0 \quad [9]$$

where μ_l and μ_v [J.kg⁻¹] are the chemical potentials of VOC in the liquid and gas phase respectively. The chemical potential of VOC in the vapour phase is expressed as (Guggenheim, 1965):

$$\mu_v = \mu_0(T) + \frac{RT}{M} \ln p_v \quad [10]$$

According to the fundamental property of the chemical potential, at constant temperature, the chemical potential of a liquid constituent is equal to the chemical potential of its vapour at equilibrium (Guggenheim, 1965):

$$\mu_l = \mu_v(p_v = p_{veq}) = \mu_0(T) + \frac{RT}{M} \ln p_{veq} \quad [11]$$

where p_{veq} is the partial pressure of gaseous VOC in equilibrium with the liquid constituent in the soil. With [10] and [11], entropy production [9] is written as:

$$\sigma = -\hat{\rho}_v \frac{R}{M} \ln \frac{p_v}{p_{veq}} \geq 0 \quad [12]$$

Close to thermodynamic equilibrium, the principles of linear thermodynamics of irreversible processes (De Groot and Mazur, 1984) leads to write:

$$\hat{\rho}_v = -\beta(\zeta_i) \ln \frac{p_v}{p_{veq}} \quad [13]$$

where $\beta(\zeta_i)$ is a positive function that depends on the imposed conditions characterized by the parameters noted ζ_i . The parameters ζ_i differ according to whether the convective or the diffusive case is considered. Function $\beta(\zeta_i)$ will be

experimentally studied in both cases: convective and diffusive. When p_v/p_{veq} tends toward 1 the logarithm can be linearized and [13] gives the Hertz-Knudsen relation (Eames *et al.*, 1997):

$$\hat{\rho}_v = \frac{\beta(\zeta_i)}{p_{veq}}(p_{veq} - p_v) \quad [14]$$

Using concentrations in the gas phase and relation [2], relation [14] can be written in a form deduced from a two-film model (Hoeg *et al.*, 2004):

$$\hat{\rho}_v = \frac{\beta(\zeta_i)}{C_{veq}}(C_{veq} - C_v) \quad [15]$$

where C_{veq} and C_v are the vapour concentrations corresponding to p_{veq} and p_v .

In this study, we adopt relation [13] and examine two cases: the gas phase is immobile - $\beta(\zeta_i)$ will be noted as $\beta_D(\zeta_i)$ - and the gas phase is mobile - $\beta(\zeta_i)$ will be noted as $\beta_C(\zeta_i)$.

3. Soil and VOC used in the investigation

The soil used in all experiments comes from the Hérault riverside (France). The average particle size is 60 μm . Let D_n [m] be the particle size corresponding to $n\%$ cumulative passing particles. The Hazen coefficient $C_e = D_{60}/D_{10} = 85$ and the curvature $C^d = (D_{30})^2/(D_{10}*D_{60}) = 7.35$. Therefore, the soil can be considered as a clayey-silty sand with a wide particle size distribution [Ruiz, 1998]. The soil was compacted using a hydraulic press for the diffusive experiments and using a proctor hammer for the convective experiments. In both cases, the target dry bulk density was 1500 kg/m^3 which corresponds to a porosity of 0.43. Table 1 shows the characteristics of the soil and its mineralogical composition. It is mainly composed of quartz and calcite [Ruiz, 1998]. In spite of their low proportions, clay and organic matter play a major role in the retention of the liquid phase.

Soil contamination often involves gasoline or diesel oil. To simulate these contaminants, we chose a specific organic compound: n-heptane. Its main physical characteristics are given in Table 1.

Table 1: Characteristics of soil and heptane

Soil	
Composition	Quartz 40%, calcite 45-50%, clay 10%,
Organic mater	2%
Granulometry	0-2 mm

Bulk density	1500 kg.m ⁻³
Real mass density	2650 kg.m ⁻³
Porosity	0.43
Heptane	
Formula	C ₇ H ₁₆
Molar mass	0.1 kg.mol ⁻¹
Density	675.19 kg.m ⁻³
Diffusion coefficient of vapour in air	$D_{va} = 0.824 \times 10^{-5} \text{ m}^2.\text{s}^{-1}$
Saturated vapour pressure at 30°C	$p_{vs}(30^\circ\text{C}) = 7780 \text{ Pa}$

The equilibrium properties of heptane in the soil are defined by the isotherm sorption curve linking the liquid activity $a(w_l)$ to the liquid content w_l . The liquid activity is a macroscopic representation of micro-scale interactions occurring at solid/liquid interfaces. Indeed, at low liquid content, the liquid phase is arranged in the form of adsorbed layers and liquid/gas equilibrium properties deviate from standard conditions. To account for the hygroscopic characteristic of soil, the liquid activity relates the saturated vapour pressure p_{vs} to the equilibrium vapour pressure p_{veq} observed in the atmosphere surrounding a soil sample:

$$p_{veq} = a(w_l)p_{vs}(T) \quad [16]$$

Hygroscopicity generally refers to an adsorbed water phase and has been widely used in food engineering and water resources management. However, very few experimental devices have been extended to characterize the VOC sorption characteristics. Therefore, a new specific method has been recently developed able to experimentally determine the sorption isotherm curve of a wide range of volatile liquid (Ouoba *et al.*, 2010). This method is much simpler to carry out as it relies on standard measurement devices, pressure and temperature.

Because a venting process results in a decrease of the liquid content, the desorption isotherm curve has been experimentally determined. It is represented in Figure 1 in the case of heptane adsorbed in the clayey-silty sand used in the study (Ouoba *et al.*, 2010). The desorption isotherm curve can be fairly approximated by the BET model (Brunauer *et al.*, 1938) as shown in Figure 1.

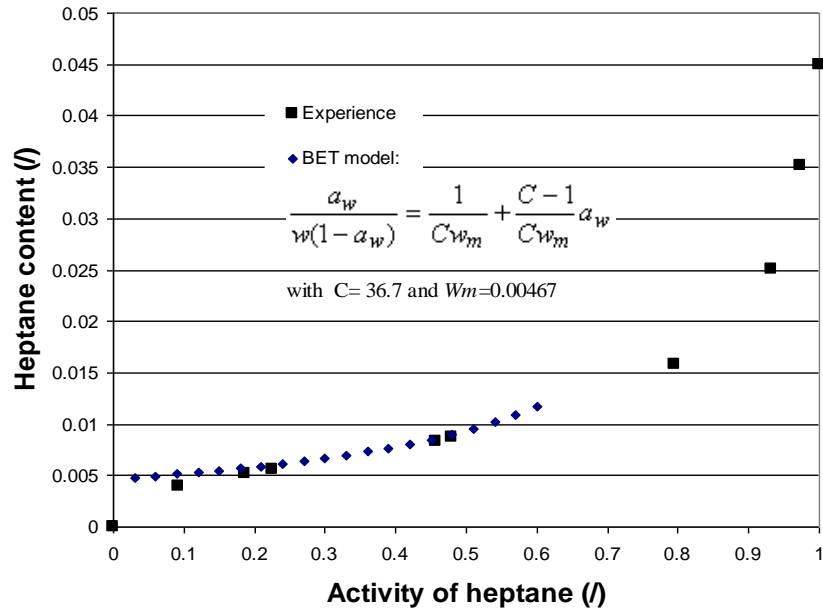


Figure 1. Desorption isotherm curve of heptane in the soil at $T = 30^{\circ}\text{C}$ (Ouoba *et al.*, 2010).

4. Phase change in the case of an immobile gas phase (diffusive case)

In this situation, VOC transfer occurs by diffusion in the gas phase. Mass flux of VOC vapour and air are equal in intensity with opposite signs. This is the case for natural attenuation or between two vapour extraction phases in intermittent treatment in the absence of convective movements induced by fluctuations in groundwater level or barometric pressure.

Relation [12] has been the subject of specific experimental characterization for water (Bénet *et al.*, 2009; Ruiz, 1998; Lozano *et al.*, 2008; Lozano *et al.*, 2009) and for heptane (Ruiz and Bénet, 2001; Chammari *et al.*, 2005). These studies showed that relation [13] correctly describes the phase change of heptane in hygroscopic soils. For a given soil, function $\beta_D(\zeta_i)$ only depends on the NAPL content, w , as described by:

$$\beta_D(w) = -\frac{R}{M}L(w) \quad [17]$$

Variation of the phase change coefficient L as a function of NAPL content has been experimentally determined and is represented in Figure 2. The experimental

method and device have been extensively detailed in previous works and will not be recalled hereafter (Lozano *et al.*, 2008; Lozano *et al.*, 2009). The new results presented in Figure 2 confirm those obtained by previous investigations (Ruiz and Bénét, 2001; Chammari *et al.*, 2005). The pattern of variation in L as a function of w was also underlined when dealing with water vaporization (Bénét *et al.*, 2009; Ruiz and Bénét, 2001). It should be associated with the liquid activity and spatial distribution of the liquid phase. The interval $[0, w_{max}]$ corresponds to the hygroscopic domain: the lower the heptane content, the stronger the binding with the soil particles (mainly with the clay fraction). This induces a decrease of the phase change rate when the NAPL content tends toward 0. In the interval $[w_{max}, w_{lim}]$, heptane behaves as in a free state. As capillary bridges develops, the evaporation surface area decreases leading to lower values of phase change coefficient L . For $w > w_{lim}$ the gas phase is occluded and phase change cannot occur.

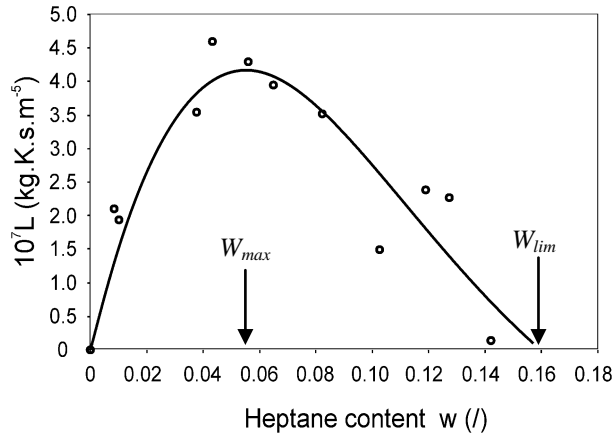


Figure 2. Phenomenological coefficient of phase change of heptane in a clayey silty sand at 30°C as a function of heptane content.

5. Phase change in the case of a mobile gas phase (convective case)

In the convective case, phase change is usually described by a first order kinetics as introduced in equation [15] (Lingineni and Dhir, 1997; Wilkins *et al.*, 1995; Rathfelder *et al.*, 2000; Yoon *et al.*, 2002):

$$\hat{\rho}_v = K(C_{veq} - C_v) \quad [18]$$

The phase change coefficient κ [$\text{kg}\cdot\text{m}^{-3}\cdot\text{s}^{-1}$] has been determined by several authors (Lingineni and Dhir, 1997; Wilkins *et al.*, 1995; Yoon *et al.* 2002). Experimental correlations are generally written as:

$$\kappa = K_o v_g^a D_g^b d_p^c \quad [19]$$

where v_g is the gas phase velocity at the pore scale, D_g the diffusion coefficient of the pollutant in the gas phase and d_p the soil particle diameter. K_o , a , b and c are case specific constants.

Coefficient κ is generally estimated from soil column experiments by measuring the vapour concentration in the gas phase c_v at the outflow of the column. This approach can be justified as long as the soil is outside its hygroscopic domain. In this case c_{veq} is independent of the liquid content and results are not affected by a liquid content gradient. In the hygroscopic domain, corresponding to lower values of liquid content, the equilibrium vapour pressure depends on the liquid content through equation [16]. Therefore, the equilibrium concentration c_{veq} cannot be defined for the whole column and equations [18] and [19] are no longer valid.

Moreover, in column experiments reported in the literature (Wilkins *et al.*, 1995; Nadim *et al.*, 1997; Yoon *et al.*, 2002), the injected gas phase is free of polluting vapour, whereas a volume of polluted soil is subjected to an airflow that is already vapour charged. Thus the coefficient is determined in conditions that are very different to what actually occurs in situ. In the following sections, an approach is proposed based on venting experiments carried out with thin layers of soil subjected to a non-polluted airflow. The proposed analysis provides a phase change relation valid for the case where the inflow is already vapour charged. Let us consider the following two cases:

- Case A: the inlet air of the soil column is free of VOC vapour;
- Case B: the inlet air of the soil column is already vapour charged.

In the following section a method is developed to evaluate $\beta_c(\zeta_i)$ in case B based on experiments carried out in case A.

5.1. Tests in thin layer VOC free inflow (case A)

5.1.1. Objectives

The purpose is to experimentally establish the remediation kinetics of soil samples in order to propose an analytical law for the evaporation rate $\hat{\rho}_v$. Experiments were carried out with thin layers submitted to an inlet airflow free of

VOC. Index A refers to this case. The hypothesis of thin layer is generally associated with the uniformity of parameters throughout the layer. Here, a weaker hypothesis is made by assuming a linear distribution of the vapour pressure throughout the thickness of the soil layer.

We demonstrate hereafter that VOC vapour content can be neglected with respect to VOC liquid content. Using the values in Table 1, heptane vapour content calculated by equation [5] is written as: $w_v = 1.14 \times 10^{-8} p_v$. Since $p_v \leq p_{vs} = 7780 \text{ Pa}$, the vapour content can be evaluated by:

$$w_v \leq 8.85 \times 10^{-5} \quad [20]$$

This calculation shows that the heptane vapour content is much lower than the global heptane content. Therefore, the liquid content w_l can be assimilated to the global heptane content w . The representative kinetics of functions $w(t)$ and $w_l(t)$ are very close to one another, and their partial derivatives remain very close throughout the experiment so:

$$w \approx w_l \text{ and } \frac{\partial w}{\partial t} \approx \frac{\partial w_l}{\partial t} \quad [21]$$

Thus, index l will no longer be mentioned.

5.1.2. Experimental setup for convective trials

Venting experiments were carried out on soil columns of 81 mm in diameter and 60 mm in thickness. Thinner samples were impossible to make due to their fragility at low liquid contents. The soil is first dried at 105°C for 24 hours. The required amounts of soil and heptane are added using a high-precision balance (10^{-3} g). Then, the soil is compacted using a Proctor hammer in order to reach a dry bulk density of 1500 kg.m^{-3} , which corresponds to a porosity of 43%. The heptane content is calculated by differential weighing after the mixing of the dry soil and the heptane. As can be seen in Figure 4, the initial heptane content was equal to 11% for $F_a = 0.077$ and $0.116 \text{ kg.s}^{-1}.\text{m}^{-2}$ and 12% for $F_a = 0,193 \text{ kg.s}^{-1}.\text{m}^{-2}$.

The synoptic scheme of the experimental setup is shown in Figure 3. Compressed air at 500 kPa was first dried to a dew point of -40°C in order to prevent water from entering the system. Air temperature was regulated at $T=30^\circ\text{C}$ and air mass inflow was controlled. The soil column was periodically removed from its support and weighed. These measurements allow the kinetics of NAPL loss to be determined.

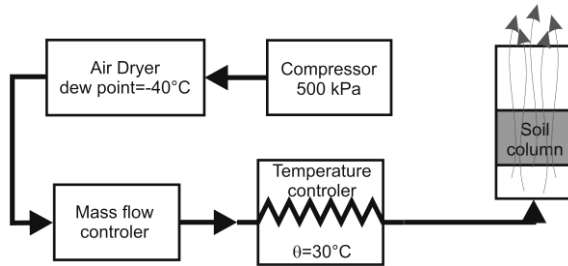


Figure 3. Synoptic scheme of the experimental setup for venting experiments.

5.1.3. Results and analysis

During a venting operation by vertical extraction wells, the gas phase velocity in the soil is inversely proportional to the distance to the well. For instance, a volumetric air flux of $0.1 \text{ m}^3 \cdot \text{s}^{-1}$ per meter length of well corresponds to a mass flux of about $0.2 \text{ kg} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$ at 0.2 m from the well axis and $0.02 \text{ kg} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$ at 1 m from the well axis. Based on these orders of magnitude, the three dry mass airflows chosen were: 0.077 , 0.116 and $0.193 \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$. On the basis of experiments at high velocity, an approach will be proposed allowing lower velocities to be considered.

The experimental global kinetics of pollutant extraction are shown by the points in Figure 4 for the three airflows.

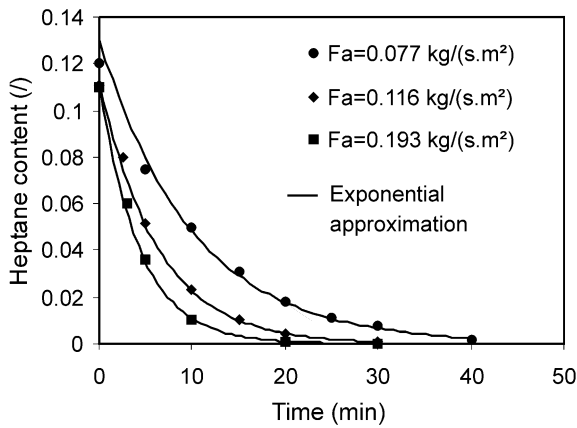


Figure 4. Experimental kinetics (points) and exponential fitting (continuous lines).

It is possible to verify that the experimental airflow range corresponds to the convective case. Indeed, the diffusive vapour flow in the air of the soil J_v [$\text{kg} \cdot \text{m}^2 \cdot \text{s}^{-1}$] is expressed as (De Vries and Kruger, 1966):

$$\mathbf{J}_v = -D_{vs} \frac{M}{RT} \nabla p_v \quad [22]$$

where D_{vs} is the diffusion coefficient of gaseous VOC in the soil. To take into account the soil tortuosity, Penman's correlation is used (Penman, 1940):

$$D_{vs} = 0.66 n_g D_{va} \quad [23]$$

where D_{va} is the diffusion coefficient of vapour in air (Table 1).

In an extreme situation the vapour pressure would vary linearly from 0 to the saturating vapour pressure (7780 Pa) along the soil column (60mm). According to [22] and [23], the diffusive vapour flow would be of the order of $2 \times 10^{-5} \text{ kg.m}^{-2}.\text{s}^{-1}$. The convective vapour flow imposed in experiments was of the order of $0.1 \text{ kg.m}^{-2}.\text{s}^{-1}$ or 10^4 times greater than the diffusive flow, which is thus fairly negligible in the experimental conditions used here.

In the case where diffusive vapour flow is negligible compared to convective flow, the gas phase velocity can be evaluated by:

$$\mathbf{v}_g = \frac{\mathbf{F}_a}{\rho_a} \quad [24]$$

where \mathbf{F}_a [$\text{kg.m}^{-2}.\text{s}^{-1}$] is the mass airflow held constant during an experiment. When the flow is unidirectional, notation F_a is used. With [24] and [5], the mass balance of gaseous VOC [7] is written:

$$\rho_s \frac{\partial w_v}{\partial t} = - \frac{n_g M}{R T \rho_a} \mathbf{F}_a \cdot \nabla p_v + \hat{\rho}_v \quad [25]$$

The total VOC mass balance is obtained by adding [7] and [25]:

$$\rho_s \frac{\partial w}{\partial t} = - \frac{n_g M}{R T \rho_a} \mathbf{F}_a \cdot \nabla p_v \quad [26]$$

Integrating [25] over a layer of thickness H , considering [1] and assuming a linear distribution of the partial VOC pressure, leads to:

$$\rho_s \frac{\partial \bar{w}}{\partial t} = - \frac{M F_a}{\rho_a^* R T} \frac{p_v(z+H) - p_v(z)}{H} \quad [27]$$

where \bar{w} is the average total VOC content in the layer; $p_v(z)$ and $p_v(z+H)$ are partial VOC pressures in z and $z+H$.

Our experiments corresponded to case A where the inlet partial vapour pressure $p_v(z)$ in relation [27] is zero. Assuming that vapour pressure and NAPL content vary linearly throughout the thickness of the layer, the average vapour pressure $(p_v)_A$ is expressed as:

$$(\overline{p_v})_A = \frac{(p_v(z+H))_A}{2} \quad [28]$$

That is to say, according to [27]:

$$(\overline{p_v})_A = - \frac{\rho_s \rho_a^* R T H}{2 M F_a} \left(\frac{\partial \bar{w}}{\partial t} \right)_A \quad [29]$$

The experimental kinetics presented in Figure 4 can be approximated by exponential functions allowing formulating the VOC mass balance as:

$$\left(\frac{\partial \bar{w}}{\partial t} \right)_A = -k(\bar{w})_A \quad [30]$$

Regarding the 3 experiments, Figure 5 shows the evolution of parameter k [s^{-1}] as a function of mass airflow F_a .

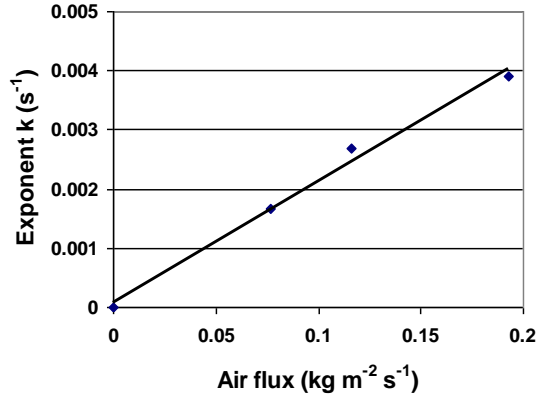


Figure 5. Representation of the parameter k versus the airflow F_a .

This figure shows that in the airflow range under investigation, a linear relation can be admitted between k and F_a . Thus, the overall phase change rate in a thin layer can be written:

$$\overline{(\hat{p}_v)}_A = -\rho_s \left(\frac{\partial \overline{w}}{\partial t} \right)_A = \rho_s \alpha \overline{(w)}_A F_a \quad [31]$$

This relation has been established in the case of a thin layer of finite thickness attacked by influent air free of VOC (case A). Ultimately they can be written as local variables in case A, and they will henceforth be used in this form. Coefficient α is the slope of the straight line in Figure 5. For study soil at $T=30^\circ\text{C}$, $\alpha = 0.0211 \text{ m}^2 \cdot \text{s}^2 \cdot \text{kg}^{-1}$.

5.2. Extension in the case of a thin layer with a mixture of air + VOC vapour (Case B)

Within a contaminated soil, an elementary volume is subjected to an airflow already charged with VOC vapour. A relation between $\overline{(p_v)}_A$ and $\overline{(w)}_A$ can be stated, according to [29] and [31]:

$$\overline{(p_v)}_A = \frac{\alpha \rho_s \rho_a^* R T H}{2M} \overline{(w)}_A \quad [32]$$

The thinner the layer, the more exact the relations [31] and [32]. A method to determine $\beta_c(\zeta_i)$ in case B from experiments conducted in case A is developed hereafter. The variables relative to this case are indexed by B.

Two experiments A and B are considered, with NAPL content w and airflow F_a identical in both cases; p_{vA} and p_v being the VOC partial vapour pressures in both experiments. It is stated that:

$$\varphi(w, F_a, p_{vA}, p_v) = \frac{(\hat{\rho}_v)_B(w, F_a, p_v)}{(\hat{\rho}_v)_A(w, F_a, p_{vA})} \quad [33]$$

where function $\varphi(w, F_a, p_{vA}, p_v)$ represents the correction to be applied to case A to obtain the phase change term in case B.

According to [37], in case A, a relation exists between the VOC content w and the VOC partial vapour pressure p_{vA} . As NAPL activity is a monotonous function of NAPL content, according to [16], one can write:

$$w = a^{-1}(p_{veq} / p_{vs}(T)) \quad [34]$$

Using [32] and [34], the set of parameters: w, F_a, p_{vA}, p_v can be replaced by: p_{veq}, F_a, p_v in [33]. At fixed F_a , correction function [33] thus only depends on two parameters:

$$\psi(p_{veq}, p_v) = \varphi(w, F_a, p_{vA}, p_v)_{F_a = \text{Constant}} \quad [35]$$

Function $\psi(p_{veq}, p_v)$ must satisfy the following conditions:

- it is a decreasing function of p_v ,
- it tends toward zero when $p_v \rightarrow p_{veq}$,
- thermodynamically, it must satisfy [12].

The function:

$$\psi(p_{veq}, p_v) = -\gamma \ln \frac{p_v}{p_{veq}} \quad [36]$$

which satisfies the above criteria, was adopted. In particular, this function is in accordance with relation [13] suggested by the analysis of entropy production. the parameter γ introduced in [36] characterize the VOC/soil configuration. It depends on the VOC physical properties, temperature, soil texture ... This parameter will be evaluated hereafter by identifying the theoretical model on experimental data.

With [31] and [36], the phase change rate [13] is written:

$$\hat{\rho}_v = -\gamma \alpha \rho_s w F_a \ln \frac{p_v}{p_{veq}} \quad [37]$$

By identifying [37] with [13], one obtains:

$$\hat{\rho}_v = -\beta_c(w, F_a) \ln \frac{p_v}{p_{veq}} \quad [38]$$

with:

$$\beta_c(w, F_a) = \gamma \alpha \rho_s w F_a \quad [39]$$

The model constituted by relations [2], [7], [25], and [37] provides a way of simulating the kinetics of a soil column and determining the fields of variables w and p_v throughout the column. A numerical model was used to accurately analyse the distribution of state variables in the 60 mm height soil columns presented in subsection 5.1. Equations [7] and [25] were discretized along the column axis using a finite difference method. The initial heptane content was uniform and equal to 11% for $F_a = 0.077$ and $0.116 \text{ kg.s}^{-1}.\text{m}^{-2}$ and 12% for $F_a = 0,193 \text{ kg.s}^{-1}.\text{m}^{-2}$ (see Figure 4). According to Figure 1, the corresponding liquid heptane activity is equal to 1, which means that the initial partial vapour pressure is equal to its saturating value (Table 1). A constant dry airflow is applied at the base of the layer. Introducing relation [37] with $\gamma=0.37$, the model gives kinetics that are totally consistent with the experiment (Figure 6). For $F_a = 0.077 \text{ kg.m}^{-2}.\text{s}^{-1}$, this model also gives the space distribution of p_v and w (Figures 7 and 8). This validates the choice of function [36] to describe the deviation effect of p_v in relation to p_{veq} .

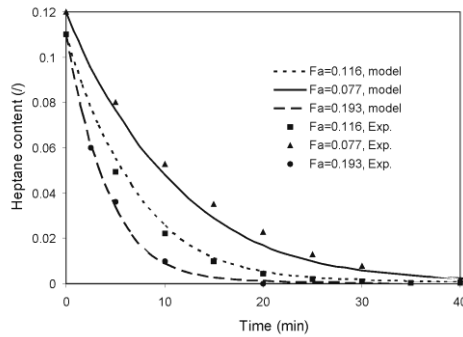


Figure 6. Comparison between experimental (points) and simulated kinetics (continuous lines).

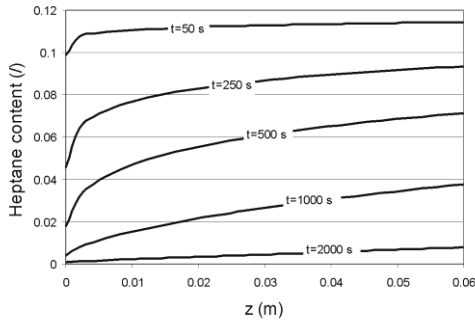


Figure 7. Time-variation of liquid content profiles in a soil column ($F_a = 0.077 \text{ kg.m}^{-2}.\text{s}^{-1}$).

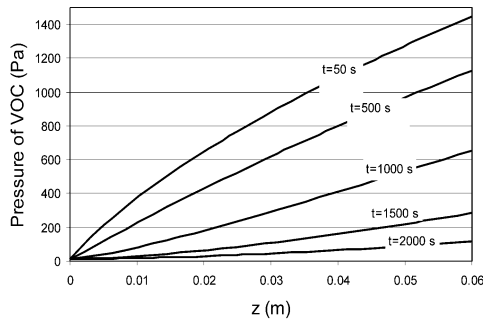


Figure 8. Time-variation of the partial pressure profiles of VOC in a soil column ($F_a = 0.077 \text{ kg.m}^{-2}.\text{s}^{-1}$).

6. Comparison between decontamination by diffusion and by convection and efficiency coefficient

By adopting the difference in chemical potential as the vaporization force caused by the thermodynamic disequilibrium between liquid VOC and its vapour, two forms of the phase change law has been established, providing a method to compare the two cases under investigation: convective and diffusive. The efficiency of convective vaporization will be quantified in comparison with diffusive vaporization using [13], [17] and [39] by the coefficient:

$$\eta(w, F_a) = \frac{(\hat{\rho}_v)_{convection}}{(\hat{\rho}_v)_{diffusion}} = \frac{\beta_c(w, F_a)}{\beta_D(w)} = \frac{\gamma \alpha \rho_s w M}{R L(w)} F_a \quad [40]$$

Below 10% NAPL content, the domain of interest here, coefficient $L(w)$ represented in Figure 2 can be approximated by:

$$L(w) = -1.25 \times 10^{-4} w^2 + 1.5 \times 10^{-5} w \quad [41]$$

According to [40], efficiency coefficient is proportional to F_a . For $\alpha = 0.0211$ and, $\gamma = 0.37$, Figure 9 shows the variation of η as a function of w for different values of F_a in the experimentally explored domain ($0.077 \text{ kg.m}^{-2}.\text{s}^{-1} \leq F_a \leq 0.193 \text{ kg.m}^{-2}.\text{s}^{-1}$). Obviously, venting efficiency tends toward 1 when F_a tends toward zero. This proposition is clearly theoretical - indeed the validity domain of the hypothesis of a negligible diffusion flow compared to the convection flow is not specified in this study. However when the efficiency coefficient is equal to 1, i.e. when the convective phase change rate equals the diffusive phase change rate, according to [40] and [41], the airflow is given by:

$$F_a = \frac{R}{\gamma \alpha \rho_s M} (-1.25 \times 10^{-4} w + 1.5 \times 10^{-5}) \quad [42]$$

For example for the studied soil with values of $w = 6\%$, $\alpha = 0.0211$ and $\gamma = 0.37$, the airflow deduced from [42] is $3.10^{-4} \text{ kg.m}^{-2}.\text{s}^{-1}$. This value is very low, and as the interest of venting is to accelerate decontamination, the airflow values used in practice are much higher than the above value. Function $\beta_C(w, F_a)$ given by [39] remains valid to simulate venting in on-site conditions. As a rough guide however, the efficiency coefficient for weak flows is represented in Figure 9.

This figure shows that airflow considerably accelerates vaporization, as an example for $F_a = 0.01 \text{ kg.m}^{-2}.\text{s}^{-1}$, the ratio [40] is in the order of 100 at low NAPL contents. In addition to vaporization associated with the difference between the chemical potentials of liquid VOC and vapour VOC, there is also vaporization under the effect of the extraction of molecules from liquid VOC due to friction between air molecules and those of liquid VOC.

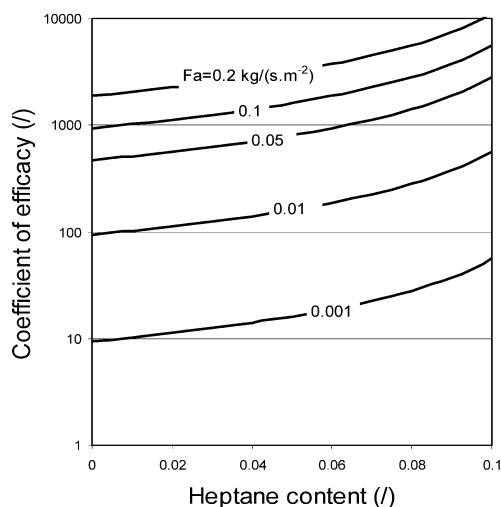


Figure 9. Variation of the efficiency coefficient versus the liquid content for various airflows.

7. Conclusions

This article presents two approaches to analyze the liquid-gas phase change phenomenon of a VOC in a hygroscopic soil. Both cases of an immobile gas phase and of a mobile gas phase are examined.

A law of VOC phase change was proposed on the basis of an experimental study in the case where the gas phase is immobile, i.e., when the transport of pollutant vapour is due to diffusion within the gas phase. This situation occurs in periods of pumping interruption or in the case of natural attenuation, in the absence of fluctuation in groundwater level or barometric pressure.

In the case of a mobile gas phase, a law of phase change was proposed from venting experiments on thin layers of soil containing liquid heptane. This law takes into account the influence of airflow and NAPL content on the rate of decontamination. This law is valid since the mass flow of the pollutant vapour is basically due to filtration of the gas phase. It is worth noting that the effect of diffusive vapour flow remains insignificant compared with the effect of convection, even for very low air velocities.

Both approaches provide a means to determine the transfer flows of the adsorbed or liquid pollutant to the gas phase. Ratios of phase change rates in the convective and diffusive cases provide a coefficient of efficiency that can be used to evaluate the contribution of venting compared with natural attenuation.

An upcoming issue is the transition from a single contaminant to a mixture (gasoline, diesel oil, petroleum, etc.). Theoretically, the equations presented above are still applicable but for the sake of rigour, each component should have its own phase change rate. However, it is possible to come down to a single equation by adding together the mass balance equations [7] and [25] and by introducing a phase change rate for the whole mixture. The experimental study of this global phase change term can be carried out using the experimental procedure described in section 5.1.2. In particular, the relation could be analysed between the phase change rate of the mixture and that of each individual component.

Naturally, the proposed approach applies to decontamination by NAPL/gas phase change and this study needs to be completed by taking into account the aqueous phase that inevitably exists in real soil. The presence of water in the medium modifies the distribution of the pollutant, part of which is dissolved and affects the transfer kinetics (Yoon *et al.*, 2002). Dissolved concentrations generally represent a small part of total pollution. But transfers between aqueous and gas phases are much slower than between NAPL and gas phase and substantially affect the efficiency of decontamination in the tailing phase. The experimental study of decontamination of a soil in the presence of water could be inspired by the experimental procedures described here and benefit from the acquired knowledge for pure water and pure heptane.

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