



ELSEVIER

Journal of Hazardous Materials 40 (1995) 237-256

**JOURNAL OF  
HAZARDOUS  
MATERIALS**

## The release into the atmosphere of hazardous volatiles Part II. Release from a slab of contaminated porous particles. The importance of free convection

Francesco Gioia\*, Fabio Murena, Giuseppe Savino

*Dipartimento di Ingegneria Chimica, Università di Napoli Federico II, Piazzale Tecchio, 80125 Napoli, Italy*

Received 27 March 1994; accepted in revised form 1 August 1994

---

### Abstract

The release of a volatile organic compound from a slab of porous particles imbued with an immobile oily phase containing the volatile is studied. The most important feature of the model is that it accounts for natural convection besides diffusion. The gas which fills the interparticle porosity of the contaminated slab has a composition, and thus a density, different from that of the surrounding atmosphere. Therefore, a natural convection flux may be established through the slab. The model shows that natural convection indeed plays an important role which increases with the vapor pressure of the component. For benzene it predominates the overall process.

---

### 1. Introduction

In the present paper the evaluation of the source emission rate of hazardous chemicals contained in porous materials is provided. The problem is of general interest in the area of chemodynamics [1]. From a more practical point of view, it finds direct application in evaluating the air emission release rate of hazardous chemicals from land treatment facilities. This problem has been carefully investigated by several authors.

Thibodeaux et al. [2] provide a review of the state-of-the-art methodology to predict the chemical vapor emission from landfills. Their modeling of the emission of volatile organic chemicals is based on the idealized single-celled source, i.e., the landfill is assumed to consist of two compartments: the lower compartment containing the source of the volatile (the waste compartment) in uniform and constant concentration; the upper compartment is the soil cover that separates the lower chamber from the

---

\* Corresponding author. Tel. (+ 39-81) 768-2277. Fax: (+ 39-81) 239-1800.

atmosphere. The authors then describe and compare four possible vapor transport mechanisms which may take place through the soil cover layer.

Karimi et al. [3, 4] provide experimental support to the theoretical framework discussed by Thibodeaux et al. [2], using a simulated landfill apparatus.

A more elaborate description of the physics of the source emission rate of hazardous chemicals is considered by the Air Emission Release Rate (AERR) model by Thibodeaux and Hwang [5]. However, some of the assumptions on which the AERR model is based may not be very realistic ones under all conditions, as discussed below. The AERR model, while postulating the existence of a moving boundary which builds up at the interface between the waste compartment and the soil cover, also assumes that at any time all solid particles in the waste compartment release the volatile, through the coating film, with the same rate. The latter assumption seems inconsistent with the existence of a moving boundary; and, indeed, Dupont [6], who tested experimentally the AERR model utilizing API separator sludge and a slop oil emulsion solids waste stream, shows that the model overestimates flux rates for the pure constituents by a factor between 2 and 10.

All the above models disregard free convection as a possible mechanism, besides diffusion, for the release of volatiles from landfills. As a matter of fact, the gas contained in the interparticle porosity has a composition, and thus a density, different from that of the surrounding atmosphere. Therefore, a natural convection flux may be established through the interparticle porosity. In the present paper a model to describe the release of volatiles from a slab of contaminated porous particles, accounting for both diffusive and natural convection fluxes, is developed. Possible scenarios to which the model could apply are piles of contaminated porous particles on the ground, or vented landfills.

## 2. Theory

We will focus attention on the case of a soil formed of particles of a natural porous material imbued with a liquid waste. The waste is formed by an oily medium of low volatility in which relatively low concentrations of toxic volatile substances are dissolved. The low volatility of the medium allows us to consider it to be immobile during the mass transfer process. In the following all quantities (porosity, concentrations, gradients, etc.) within the single porous particles are termed intraparticle, while those which prevail in the fluid surrounding the particles (inside the mass of soil) are termed interparticle.

The transport of the volatile into the surrounding environment takes place through the two series/parallel mechanisms: (i) the release of the volatile from the intraparticle porosity into the interparticle porosity of the soil layer; (ii) the transport mechanism of the volatile (as a vapor) through the interparticle porosity towards the surrounding environment by both diffusion and free convection.

In a previous paper (henceforth called Part I) Gioia et al. [7] have investigated, both theoretically and experimentally, the release of different volatiles, having a large range of volatilities, from the intraparticle porosity of porous spheres which were

imbued with the waste. The release takes place through two mechanisms in series. The first is the diffusion in the porous particles (filled with the oily phase) towards their external surface. The second is the transport through the gas film surrounding the particles. The Biot number is the indicator of which of the two resistances (internal, i.e., within the macropore structure of the spheres, or external, i.e., across the gas film surrounding the spheres) controls the diffusion of volatile from liquid to gas. In particular, as shown in Part I it is possible to infer that for  $Bi \leq 1$ , it is a good approximation to assume that external resistance controls the diffusion process. In this instance the concentration profiles in the particle remains flat ( $c(R) \approx c(r = 0)$ ). On the other side, when  $Bi \gg 1$  (say  $Bi \geq 10$ ) internal resistance prevails ( $c(R) \approx 0$ ). The Biot number is calculated by

$$Bi = \frac{K_m R}{\frac{D_s}{q}}, \quad (1)$$

where  $K_m$  is the gas phase mass transfer coefficient.

It is important to note that  $K_m$  must be referenced to liquid-phase concentrations. Namely, if  $K_g$  is the gas-phase mass transfer coefficient, with reference to gas-phase concentrations (as calculated by the usual correlations),  $K_m$  is related to  $K_g$  by the following equation:

$$K_m = K_g \frac{p^v}{\mathcal{R} T c_l}. \quad (2)$$

Inspection of Eqs. (1) and (2) shows that the Biot number varies according to the volatility of the compound. Therefore, as the volatility decreases, a greater role is played by external resistance in controlling the diffusion process. As an example it was shown in Part I that when benzene, chlorobenzene and dichlorobenzene are simultaneously present in the liquid mixture imbuing the porous particles ( $R = 2.2$  mm), the diffusion of benzene ( $p^v = 75$  mmHg @  $19^\circ\text{C}$ ) is internally controlled, that of chlorobenzene ( $p^v = 8.4$  mmHg @  $19^\circ\text{C}$ ) is under a mixed control while that of dichlorobenzene ( $p^v = 1.5$  mmHg @  $19^\circ\text{C}$ ) is externally controlled.

### 2.1. Modeling the release from a slab of contaminated porous particles

The results obtained in Part I give us the tools to predict with confidence the release mechanism from any porous particle which forms the slab. Therefore, it is possible to develop a model for the release of the volatile to the environment from the whole slab. In developing this model we will take into consideration both the diffusion and the free convection processes.

We will consider the slab to be formed by porous particles imbued with an oily phase in which a single toxic volatile compound is dissolved. Furthermore, we assume that the slab is vented to the atmosphere at the bottom. The existence of venting at the bottom is prerequisite for a natural convection flux to establish through the slab.

Possible scenarios to which the model could apply are piles of contaminated porous particles laying on the ground, or vented landfills. A pile has a conical or flat-topped

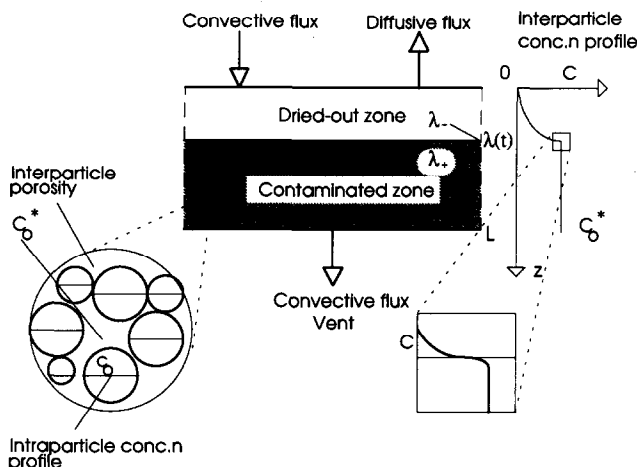


Fig. 1. Schematic model of natural convection and diffusion fluxes in a slab of contaminated porous particles. Sketch of the concentration profiles in the particles and in the slab.

shape. Thus, a three-dimensional model would be necessary to describe its behavior. To simplify the analysis and to obtain simple equations predicting the release rate of the volatile compound, we consider a pile having the shape of a slab, the length and the width of which are much larger than its height. Naturally the slab approximation fits quite realistically in the case of a landfill.

For the case of the pile the lower part of the side surface plays the role of the bottom venting. A landfill may be considered to be vented at the bottom if a leachate collection/removal piping system exists underneath the waste and the vent outlet is at the bottom level. In both cases the release process is dealt with by a one-dimensional model that accounts only for vertical variations of the variables.

We set the  $z$  axis along the direction of gravity (perpendicular to the top and bottom face of the slab) with the origin at the top. We will show that the release process is a moving boundary problem. This boundary separates the lower contaminated part of the slab from the upper part (the dried-out zone) which has become free of volatiles. We define as  $\lambda(t)$  the position of the moving boundary at any time  $t$ . We assume that at the bottom of the slab ( $z = L$ ) a vent exists. A schematic view of the geometry of the system is as in Fig. 1.

In order to model the process we have to write four equations:

- Two differential mass balance equations for the volatile component on the gas phase which fills the interparticle porosity, the first in the dried-out zone and the second in the contaminated zone. These equations will allow us to obtain the gas-phase concentration profiles of the volatile compound in both zones. These profiles are the prerequisite to evaluate the diffusive fluxes leaving the slab at the top face and to determine the overall density of the gas phase. This density regulates the natural convection velocity through the soil.

– An overall momentum balance is written to evaluate the natural convection velocity.

– A differential mass balance equation for the volatile component on the liquid phase which fills the intraparticle porosity in order to evaluate the velocity of the moving boundary.

#### Mass balances in the gas phase

The differential mass balances for the volatile component in the dried-out zone and in the contaminated zone are, respectively:

$$D_{pa} \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} = \varepsilon_p \frac{\partial C}{\partial t} \quad \text{for } 0 < z \leq \lambda(t), \quad (3)$$

$$D_{pb} \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} = \varepsilon_p \frac{\partial C}{\partial t} - K_g a_v (C_i^* - C) \quad \text{for } \lambda(t) \leq z < L. \quad (4)$$

$C(t, z)$  is the concentration of the volatile component in the gas phase and  $u$  is the superficial free convection velocity; i.e., the velocity through the total slab cross-sectional area. For the geometry we are dealing with, the velocity  $u$  is constant with  $z$ .  $C_i^*(t, z)$  is the gas-phase concentration that would be in equilibrium with the liquid-phase concentration of the volatile component at the gas/particle interface; i.e., at  $r = R$ ,  $z$ , and  $t$ .  $K_g$  is the gas-phase mass transfer coefficient and  $a_v$  is the specific interfacial area in the slab.  $\lambda(t)$  is the position of the moving boundary measured from the top of the slab (see Fig. 1).  $D_{pa}$  and  $D_{pb}$  are the effective diffusion coefficients in the dried-out zone and in the contaminated zone, respectively. They are defined as:

$$D_p = \frac{D_a \varepsilon_p}{q_p}. \quad (5)$$

The first term on the left-hand side of both Eqs. (3) and (4) is the diffusive contribution to the flux. The second is the free convection contribution. We are studying the case in which the volatile component has a molecular weight higher than that of air. This is the case which would be mostly encountered when the contaminants are hazardous chemicals. Therefore, the free convection velocity  $u$  is directed downwards while the diffusive flux is directed upwards. The last term on the right-hand side of Eq. (4) is the flux of the volatile component leaving the particles (from the liquid phase to the gas phase).

In order to avoid a numerical solution of the above equations which would be of limited practical use, Eqs. (3) and (4) may be markedly simplified by making the following physically sound assumptions:

– The accumulation term  $\partial C / \partial t$  has been included in both equations because the release process is by its nature a transient phenomenon. However, due to the slow movement of the boundary it is reasonable to assume quasi-steady-state conditions [8]. This allows us to neglect the accumulation term in both equations, which, thus,

reduce to ordinary differential equations. The time dependence of the process will be introduced through  $\lambda(t)$ .

– In many practical cases,  $Bi \leq 1$ . Therefore, as discussed in Part I, it may be safely assumed that the release from the particles is controlled by external resistances. Consequently the concentration profiles in the liquid phase inside the particles are flat. Therefore in Eq. (4),  $C_i^*$  is the gas-phase concentration that would be in equilibrium with the liquid-phase concentration of the volatile component in the whole particle.

– The contaminated zone (starting from  $\lambda(t)$  downwards) works like a packed bed desorber. The efficiency of the desorption process may be characterized by the number of transport units (NTU):

$$NTU = \frac{K_g a_v (L - \lambda)}{u} \quad (6)$$

Values of  $a_v$  and  $L$  typical for piles of incoherent materials make  $NTU \gg 1$  during all the release process. This means that in the contaminated zone the concentration of pollutant in the gas phase reaches the saturation value in just a narrow portion of the total height of the pile starting from  $\lambda(t)$ , i.e., only the particles close to the boundary release the volatile component. Therefore, the concentration profile in the liquid phase may be assumed to be a step function on  $\lambda(t)$ . Consequently,  $C_i^*$  in Eq. (4) may be assumed to be the gas-phase concentration in equilibrium with the initial liquid concentration  $c_0$ , which, for  $z > \lambda(t)$ , is constant with time and  $z$ ; i.e.,  $C_i^* \cong C_0^*$ . Preliminary calculations have shown that this is a sound assumption.

With the above assumptions we can rewrite Eqs. (3) and (4), respectively, as

$$D_{pa} \frac{d^2 C}{dz^2} - u \frac{dC}{dz} = 0 \quad \text{for } 0 < z \leq \lambda(t), \quad (7)$$

$$D_{pb} \frac{d^2 C}{dz^2} - u \frac{dC}{dz} = -K_g a_v (C_0^* - C) \quad \text{for } \lambda(t) \leq z < L. \quad (8)$$

#### Overall momentum balance

The difference of density between the gas phase in the slab and the external air generates a convective flux which is directed downward since we are considering pollutants heavier than air. Because at the bottom and at the top the pressure equals atmospheric pressure, the convective flow of the gas through the slab is due to the weight difference between the gas in the slab and the external air. Therefore the overall momentum balance, neglecting the term due to the change of kinetic energy, is:

$$\int_0^L \rho g \, dz - \rho_a g L = \Delta P_f, \quad (9)$$

where  $\rho$  is the density of the gas in the interparticle porosity,  $\rho_a$  is the atmospheric density,  $g$  is the standard gravity and  $\Delta P_f$  represents the friction losses in the slab.

*Mass balance on the liquid phase*

Having assumed that the liquid-phase concentration is a step function, the movement of the boundary with time, i.e., the variation law of  $\lambda$  with  $t$ , is given by the following mass balance for the volatile compound on the liquid phase:

$$\frac{d\lambda}{dt}(1 - \varepsilon_p)\varepsilon C_0 = N_c - N_d, \quad (10)$$

where  $(1 - \varepsilon_p)$  is the volume fraction of the pile occupied by the solid phase and  $\varepsilon$  is the intraparticle porosity;  $N_c$  and  $N_d$  are, respectively, the convective and the diffusive flux of the volatile leaving the pile, the first from the bottom face the second from the top face. Again, the minus sign for  $N_d$  is due to the fact that the diffusive flux has a direction opposite to  $z$ , while  $N_c$  is directed in the positive  $z$  direction.

*Boundary conditions for Eqs. (7) and (8)*

$$\text{For } z = 0 \quad C = 0, \quad (11)$$

$$\text{for } z = \lambda(t) \quad uC(\lambda_-) - D_{pa} \left. \frac{dC}{dz} \right|_{\lambda_-} = uC(\lambda_+) - D_{pb} \left. \frac{dC}{dz} \right|_{\lambda_+}, \quad (12)$$

$$\text{For } z = \lambda(t) \quad C(\lambda_-) = C(\lambda_+), \quad (13)$$

$$\text{For } z = L \quad \frac{dC}{dz} = 0. \quad (14)$$

The first condition, Eq. (11), is based on the consideration that the resistance to mass transfer from the top face of the slab to the atmosphere is negligible with respect to the internal one, even for very low values of wind speed. Consequently, assuming that the concentration of the pollutant in the atmosphere is very low ( $\approx 0$ ) boundary condition (b.c.) (11) holds true.

The second and the third conditions, Eqs. (12) and (13), state the continuity of the flux and of the concentration  $C$  at the moving boundary (at  $z = \lambda(t)$ ). Both Eqs. (12) and (13) are in agreement with the conditions suggested by Wehner and Wilhelm [9].

The last condition, Eq. (14), states that the diffusive flux is zero at the bottom surface. It is a consequence of having assumed that the gas-phase concentration is constant and equal to  $C_0^*$  throughout all the contaminated zone (except in the limiting case of  $\lambda(t) \approx L$ ). A discussion on the validity of condition (14) is reported by Wehner and Wilhelm [9].

*Initial condition for Eq. (10)*

$$\text{For } t = 0 \quad \lambda = 0. \quad (15)$$

**3. Solution of the equations**

The procedure that will be followed to solve the above set of equations (with the initial and boundary conditions) may be summarized as follows: First Eqs. (7) and (8),

which are coupled through the boundary conditions (11)–(14), are solved. The solution of these two equations gives the gas-phase concentration profiles in the two zones of the slab as a function of  $z$ ,  $u$  and  $\lambda$  (which is introduced by the boundary conditions, Eqs. (12) and (13)). Then by Eq. (9)  $u$  is obtained as a function of  $\lambda$ . Finally Eq. (10) is solved giving  $\lambda$  as function of  $t$ . At this stage all quantities of interest (fluxes, concentration profiles, etc.) can be obtained as a function of  $t$  which is the variable of interest.

### 3.1. Solution of Eqs. (7) and (8)

We assume that the pore structure characteristics of both contaminated and dried-out zones are the same. Therefore:  $D_{pa} = D_{pb} = D_p$ . To solve these equations it is suitable to introduce the following dimensionless numbers and variables:

$$Pe = \frac{u \times (L - \lambda(t))}{D_p}, \quad (16)$$

$$Q = \frac{K_g a_v}{u} (L - \lambda(t)) \equiv NTU, \quad (17)$$

$$\zeta = \frac{z - \lambda(t)}{L - \lambda(t)}, \quad (18)$$

$$\Gamma = 1 - \frac{C}{C^*}. \quad (19)$$

The meaning of the above dimensionless quantities is as follows:  $Pe$  is the Peclet number referred to the contaminated zone;  $Q$  is an evaporation group equivalent to the reaction group defined by Wehner and Wilhelm [9];  $\zeta$  is a dimensionless coordinate which has its origin at  $z = \lambda(t)$ ;  $\Gamma$  is a dimensionless concentration.

By introducing these dimensionless parameters, Eqs. (7) and (8) become

$$\frac{1}{Pe} \frac{d^2 \Gamma}{d\zeta^2} - \frac{d\Gamma}{d\zeta} = 0 \quad \text{for } \zeta \leq 0, \quad (20)$$

$$\frac{1}{Pe} \frac{d^2 \Gamma}{d\zeta^2} - \frac{d\Gamma}{d\zeta} - Q\Gamma = 0 \quad \text{for } 0 \leq \zeta < 1, \quad (21)$$

the boundary condition (11) becomes

$$\text{For } \zeta = \frac{-\lambda(t)}{L - \lambda(t)} \quad \Gamma = 1. \quad (22)$$

In the assumption that  $D_{pa} = D_{pb}$  the boundary condition (12), accounting for condition (13), can be written as

$$\text{For } \zeta = 0 \quad \left. \frac{d\Gamma}{d\zeta} \right|_{0^-} = \left. \frac{d\Gamma}{d\zeta} \right|_{0^+}. \quad (23)$$



Finally the b.c.'s (13) and (14) become

$$\text{For } \zeta = 0 \quad \Gamma(0_-) = \Gamma(0_+), \tag{24}$$

$$\text{For } \zeta = 1 \quad \frac{d\Gamma}{d\zeta} = 0. \tag{25}$$

The exact solution of the set of Eqs. (20) and (21) with b.c.'s (22)–(25) is reported in the appendix. For the case of the release of volatiles from contaminated soils the numerical values of the parameters are such that a much simpler solution is possible. Let us consider the quantities:

$$a = \sqrt{1 + \frac{4Q}{Pe}} \quad \text{and} \quad Pe \times a, \tag{26}$$

where  $Q$  and  $Pe$  are defined by Eqs. (16) and (17). In practical cases (see for example Table 3) values of  $Q \gg Pe$  are the rule. Therefore:  $a \gg 1$ . Furthermore, it is also found that  $Pe \times a \gg 1$  (the limiting case  $\lambda \rightarrow L$  which corresponds to  $Pe \rightarrow 0$  will be dealt within a specific section). Introducing the conditions  $a \gg 1$  and  $Pe \times a \gg 1$  the exact solution of Eqs. (20) and (21) may simplified as follows:

$$\Gamma = \frac{1 - \exp(Pe \zeta)}{1 - \exp\left(-\frac{u\lambda(t)}{D_p}\right)} \quad \text{for } \zeta \leq 0, \tag{27}$$

$$\Gamma = \frac{2\left\{\exp\left[Pe \times a \left(\frac{\zeta}{2} - 1\right)\right] + \exp\left(-Pe \times a \frac{\zeta}{2}\right)\right\}}{a \left[1 - \exp\left(-\frac{u\lambda(t)}{D_p}\right)\right]} \quad \text{for } 0 \leq \zeta < 1. \tag{28}$$

Returning to the dimensional variables, from Eq. (27) we obtain

$$C(z) = C_0^* \left[ \frac{1 - \exp\left(\frac{u(z - \lambda(t))}{D_p}\right)}{1 - \exp\left(-\frac{u\lambda(t)}{D_p}\right)} \right] \quad \text{for } 0 < z \leq \lambda(t). \tag{29}$$

From Eq. (29) the diffusive flux leaving the top surface of the slab is

$$N_d = -D_p \frac{dC}{dz} \Big|_{z=0} = \frac{uC_0^*}{1 - \exp\left(-\frac{u\lambda(t)}{D_p}\right)}. \tag{30}$$

The convective flux leaving the bottom of the pile through the vents is simply

$$N_c = uC_0^*. \tag{31}$$

### 3.2. Limiting cases

The values  $\lambda = 0$  and  $\lambda = L$  deserve specific consideration. For  $\lambda = 0$  Eq. (30) gives a value of  $N_d = \infty$ . This result is a consequence of boundary condition (11). When  $\lambda(t) \rightarrow 0$  this b.c. is no longer physically sound. In fact the external (top surface/atmosphere) resistance controls the flux of the volatile pollutant. In this case the flux can be simply expressed by

$$N_d = K_{ex} C_0^*, \quad (32)$$

where the external mass transport coefficient  $K_{ex}$  can be evaluated by a correlation like that reported by Mackay and Matsugu [10] (see Eq. (43)). However, starting from  $\lambda = 0$ , after a time  $t_i$  the moving boundary reaches a penetration depth  $\lambda(t_i) = \lambda_i$  such that the mass transport to the atmosphere becomes controlled by internal resistances. From this time on Eqs. (29) and (30) hold true. A good estimate of  $\lambda_i$  may be obtained assuming that the internal control starts when  $Bi_{ex} = 10$ .  $Bi_{ex}$  is the Biot number defined at the atmosphere/slab interface. Thus

$$\lambda_i = \frac{10D_p}{K_{ex}}. \quad (33)$$

When  $\lambda \rightarrow L$ ,  $Pe \rightarrow 0$  and  $Pe \times a \gg 1$  is no longer true and Eqs. (29) and (30) are no longer valid. We define  $\lambda_r$  as the penetration depth beyond which the condition  $Pe \times a \gg 1$  is no longer true.

On the basis of the previous considerations it may be inferred that Eqs. (29) and (30) are valid only in the range  $\lambda_i \leq \lambda \leq \lambda_r$ . However, the values of the parameters which define both  $\lambda_i$  and  $\lambda_r$  (see Table 2) are such that both  $\lambda_i/L$  and  $(L - \lambda_r)/L$  are much smaller than unity. Therefore, apart from the very beginning (where the flux can be calculated by Eq. (32)) and the very end of the process, Eqs. (29) and (30) can be safely used to describe the release process.

### 3.3. Solution of Eq. (9)

Using the ideal gas law the difference between the density of the gas phase in the slab and that of the atmosphere can be calculated by

$$\rho - \rho_a = C(z) \times (M - M_a). \quad (34)$$

The friction loss  $\Delta P_f$  in Eq. (9) can be defined as

$$\Delta P_f = \frac{2Lf\rho u^2}{2R}, \quad (35)$$

where, for the friction factor  $f$ , the Blake-Kozeny equation is used [11]

$$f = \left( \frac{(1 - \varepsilon_p)^2}{\varepsilon_p^3} \right) \frac{75\mu}{2R\rho u}. \quad (36)$$

By introducing the permeability,

$$k = \frac{4R^2\varepsilon_p^3}{150(1 - \varepsilon_p)^2}, \quad (37)$$

the friction loss becomes

$$\Delta P_f = \frac{L\mu u}{k}. \quad (38)$$

Considering that in the dried-out zone ( $z < \lambda(t)$ ) the gas-phase concentration is a function of  $z$  while in the contaminated zone ( $z > \lambda(t)$ ) it is constant and equal to  $C_0^*$ , Eq. (9) may be written as

$$\int_0^{\lambda(t)} (\rho - \rho_a)g \, dz + (\rho - \rho_a)|_{z>\lambda} g(L - \lambda(t)) - \frac{\mu u L}{k} = 0. \quad (39)$$

$\rho - \rho_a$  under the integral is Eq. (34) with  $C(z)$  given by Eq. (29), while  $(\rho - \rho_a)|_{z>\lambda}$  is still given by Eq. (34) but with  $C(z) = C_0^*$ .

The solution of Eq. (39) gives the relationship between  $u$  and  $\lambda$ :

$$u = \frac{kg(M - M_a)C_0^*}{\mu} \times \frac{L_c}{L}, \quad (40)$$

where

$$L_c = L - \frac{\lambda(t) - \frac{D_p}{u} \left[ 1 - \exp\left(\frac{u(z - \lambda(t))}{D_p}\right) \right]}{1 - \exp\left(-\frac{u\lambda(t)}{D_p}\right)}. \quad (41)$$

The convective velocity  $u$  calculated by Eq. (40) accounts only for the difference of density due to the different composition of the air and of the gas in the slab. However, it must be pointed out that temperature differences between the inside and the outside of the slab also could generate convective flows.

### 3.4. Solution of Eq. (10)

The relationship between time and position of the moving boundary can be calculated from Eq. (10) in which  $N_d$  is expressed by Eq. (30) and  $N_c$  by Eq. (31):

$$t = (1 - \varepsilon_p)\varepsilon c_0 \int_0^{\lambda} \frac{1}{uC_0^*} \left[ 1 - \exp\left(-\frac{u\lambda}{D_p}\right) \right] d\lambda. \quad (42)$$

### 3.5. Calculation procedure

In order to calculate the release fluxes  $N_d$ ,  $N_c$ , and the gas-phase concentration profiles as a function of time, the following procedure may be adopted: a value of  $\lambda$  is

fixed. By trial and error Eqs. (41) and (40) are solved to find the corresponding value of  $u$ . Then, by Eqs. (29)–(31) the concentration profile in the dried-out zone and the release fluxes are calculated. The procedure is repeated with other  $\lambda$  values. Thus obtaining fluxes and concentrations vs.  $\lambda$ . Finally, the relationship between time and  $\lambda$  may be obtained by solving Eq. (42) numerically.

#### 4. Simulations

In this section, as an example, three simulations of emission of toxic organic pollutants from a slab (vented at the bottom) of a contaminated soil are carried out. The geometry of the system is that reported in Fig. 1. The simulation is based on the equations previously developed.

The assumed internal and external geometric characteristics of the contaminated soil are:  $R^r = 0.05$  cm (particles radius);  $\varepsilon = 0.38$  (intraparticle porosity);  $L = 200$  cm (slab height);  $\varepsilon_p = 0.4$  (slab porosity);  $q_p = \sqrt{2}$  (slab tortuosity);  $a_v = 16.7$  cm<sup>2</sup>/cm<sup>3</sup> (specific interparticle area).

As a rule of thumb the tortuosity has been assumed to be  $\sqrt{2}$  in the interparticle voidage of unconsolidated particles.

Three wastes are considered. Each waste contains only one volatile pollutant of 0.1 molar concentration in tetradecane. The volatile pollutants which have been chosen are benzene, chlorobenzene and 1,3-dichlorobenzene which cover a large spectrum of volatilities. Tetradecane was chosen as solvent medium for its very low volatility which lets us consider it practically immobile. In Table 1 the physical properties at 19 °C and the initial concentrations in liquid phase of the volatiles are reported.

Firstly we calculate by Eq. (33) the lower limit  $\lambda_i$  of validity of the proposed model. The external mass transfer coefficient  $K_{ex}$  is evaluated with the Mackay and Matsugu [10] correlation:

$$K_{ex} = 0.482v_x^{0.78}d^{-0.11}Sc^{-0.67}. \quad (43)$$

Assuming a wind velocity ( $v_x$ ) 10 m/s and a width ( $d$ ) of 10 m the  $\lambda_i/L$  values reported in Table 2 are obtained. It may be observed that these values are much smaller than unity. The values of the time  $t_i$  reported in Table 2 correspond to the time

Table 1  
Physical properties (@  $T = 19^\circ\text{C}$ ) of pollutants and total liquid-phase concentration

Volatile pollutant	Vapor pressure, $p^v$ (bar)	Diffusivity in air, $D_a$ (cm <sup>2</sup> /s)	Total liq. conc., $c_i$ (mol/ml)	Molecular weight, $M$
Benzene	$9.96 \times 10^{-2}$	$8.57 \times 10^{-2}$	$4.13 \times 10^{-3}$	78
Chlorobenzene	$1.12 \times 10^{-2}$	$7.76 \times 10^{-2}$	$4.11 \times 10^{-3}$	112
1,3-Dichlorobenzene	$2.07 \times 10^{-3}$	$7.02 \times 10^{-2}$	$4.09 \times 10^{-3}$	147

Table 2  
Mass transport coefficients, Biot numbers and validity range of the proposed model

Volatile pollutant	$K_{ex}$ (cm/s)	$K_g$ (cm/s)	$\lambda_i/L$	$\lambda_r/L$	$t_i$ (min)	$t_r$ (years)	$Bi$
Benzene	1.52	0.49	$8.0 \times 10^{-4}$	0.998	1	1.8	1.60
Chlorobenzene	1.42	0.44	$7.5 \times 10^{-4}$	0.988	91	38.6	0.25
1,3-Dichlorobenzene	1.33	0.40	$7.5 \times 10^{-4}$	0.988	512	296.7	0.04

necessary for the moving boundary to reach the  $\lambda_i$  position. They have been calculated using, in the liquid phase mass balance (Eq. (10)), Eq. (32) rather than Eq. (30) for the diffusive flux  $N_d$ .

The value of the mass transfer coefficient  $K_g$ , reported in Table 2 has been calculated by the correlation suggested by Pinto et al. [12] which, due to the low values of the natural convection velocity, reduces to

$$\frac{Sh}{\varepsilon_p} = \frac{2RK_g}{D_p} = 2. \quad (44)$$

As discussed before, Eqs. (27) and (28) are not valid when  $Pe \times a$  is not much larger than unity. The penetration depth  $\lambda_r$ , beyond which the condition  $Pe \times a \gg 1$  is not true anymore, is calculated setting the condition  $Pe \times a = 10$ . The resulting values of  $\lambda_r$  are reported in Table 2. It can be observed that in practice  $\lambda_r \approx L$ .

It is useful to check on the correctness of the hypothesis on which the liquid mass balance equation (10) is based; i.e., the concentration profile along  $z$  in the contaminated zone, may be approximated by a step function on the moving boundary. This condition is valid as long as the dimensionless group  $NTU \gg 1$ . Inspection of Table 3 shows that in all cases the condition  $NTU \gg 1$  is satisfied.

## 5. Results of simulation and discussion

The results of the simulation are reported in Figs. 2 and 3. In Fig. 2 the dimensionless  $C/C_0^*$  concentration profiles vs. the dimensionless coordinate  $z/L$  along the height of the soil slab for the three simulation cases; i.e., mixtures in tetradecane of: benzene (Fig. 2(a)); chlorobenzene (Fig. 2(b)); 1,3-dichlorobenzene (Fig. 2(c)), are reported. For all three mixtures the initial concentration is 0.1 molar fraction.

The labels on the curves are the elapsed dimensionless times  $\tau = t/t_r$  from the beginning of the release process.

The points where the curves reach a value of the ordinate equal to one is the instantaneous position of the moving boundary. On the left side of this point lies the dried-out zone, on the right the contaminated zone. Again one should note that in

Table 3  
Characteristic parameters

Volatile pollutant	$\lambda_i/L^a$	$u$ (cm/s)	$Pe$	$Q \equiv NTU$	$a$	$Pe \times a$
Benzene	$\lambda_i/L$	$1.34 \times 10^{-3}$	11.03	$1.21 \times 10^6$	662	7301
	0.1	$1.26 \times 10^{-3}$	9.34	$1.16 \times 10^5$	705	6585
	0.5	$8.43 \times 10^{-4}$	3.47	$9.63 \times 10^5$	1038	3601
	0.9	$4.51 \times 10^{-4}$	0.37	$3.6 \times 10^5$	1970	730
Chlorobenzene	$\lambda_i/L$	$2.56 \times 10^{-4}$	2.32	$5.74 \times 10^6$	3146	7298
	0.1	$2.43 \times 10^{-4}$	1.98	$5.44 \times 10^6$	3315	6563
	0.5	$1.83 \times 10^{-4}$	0.83	$4.01 \times 10^6$	4396	3648
	0.9	$1.22 \times 10^{-4}$	0.11	$1.20 \times 10^6$	6618	728
1,3-Dichlorobenzene	$\lambda_i/L$	$6.70 \times 10^{-5}$	0.67	$1.95 \times 10^7$	10,789	7228
	0.1	$6.36 \times 10^{-5}$	0.57	$1.85 \times 10^7$	11,374	6506
	0.5	$4.95 \times 10^{-5}$	0.25	$1.32 \times 10^7$	14,591	3618
	0.9	$3.52 \times 10^{-5}$	0.04	$3.72 \times 10^6$	20,620	7217

<sup>a</sup> Values of  $\lambda_i/L$  are in Table 2.

agreement with one of the assumptions of the model, in the contaminated zone the concentration profiles are flat and the gas-phase concentration may be assumed to be equal to  $C_0^*$ . Furthermore, the curvature of the profiles in the dried-out zone (which is related to the value of  $u$ ) decreases as the volatility of the compound decreases. For the less volatile compound, 1,3-dichlorobenzene, the profiles are practically linear.

In Fig. 3 the release fluxes of the volatile component, for the same set of mixtures as in Fig. 2 (in the same order), are reported vs. time.  $N_d$  and  $N_c$  are the diffusive and the convective fluxes, respectively. The first leaving the slab from the top face, the second through the vent at the bottom.  $N_t$  is the sum of the two fluxes. One should note that the volatility of the component plays a major role on the convective flux rather than on the diffusive one. In fact for the most volatile component (benzene, Fig. 3(a))  $N_c$  is of the order of  $10^{-10}$  while, for the least volatile one (1,3-dichlorobenzene, Fig. 3(c)), it is of the order of  $10^{-13}$ . In particular, observing the  $N_t$  curves, it is apparent that for benzene the release mechanism is essentially free convection. The situation is reversed for dichlorobenzene. This result has a sound physical meaning. In fact, the free convection flux is determined by the difference between the density of the gas phase inside the slab and that of the outside air. When the vapor pressure of the compound decreases, its content in the gas phase becomes smaller and the driving force for the free convection decreases. The 1,3-dichlorobenzene, even though it has a molecular weight which is 1.9 times larger than that of the benzene, generates a convective flux much smaller because it has a vapor pressure that is about 50 times smaller. The behavior of multicomponent mixtures is beyond the scope of this paper, however, we can predict that for such mixtures the convective flux would be regulated by the most volatile component.

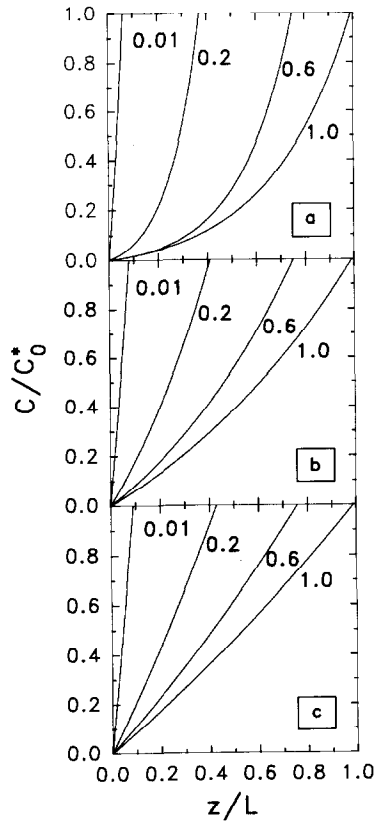


Fig. 2. Concentration profiles in the slab as obtained from the simulation calculations. The labels on the curves are the dimensionless times  $\tau$  from the beginning of the release process: (a) benzene in tetradecane; (b) chlorobenzene in tetradecane; (c) 1,3-dichlorobenzene in tetradecane. For all three mixtures the initial concentration of the volatile compound is 0.1 mol fraction.

Naturally, volatility plays a role also on the diffusive flux. In fact, more volatile compounds have steeper concentration profiles in the dried-out zone.

The slight increase that  $N_d$  undergoes at the end of the release process for the case of benzene is explained as follows: When the release process reaches the end, the convective velocity becomes very small and the curvature of the concentration profile in the dried-out zone decreases. For  $u = 0$  the profiles must be linear. A decrease in the curvature makes the slope (and then the flux) at  $z = 0$  larger. Inspection of Fig. 4, which is an enlargement of Fig. 2(a) around the origin, indeed shows that the curve for  $\tau = 1$  crosses that for  $\tau = 0.6$  and has a larger slope at  $z = 0$ . This phenomenon is not detected for the less volatile compounds which have convective velocities much smaller than that of benzene.

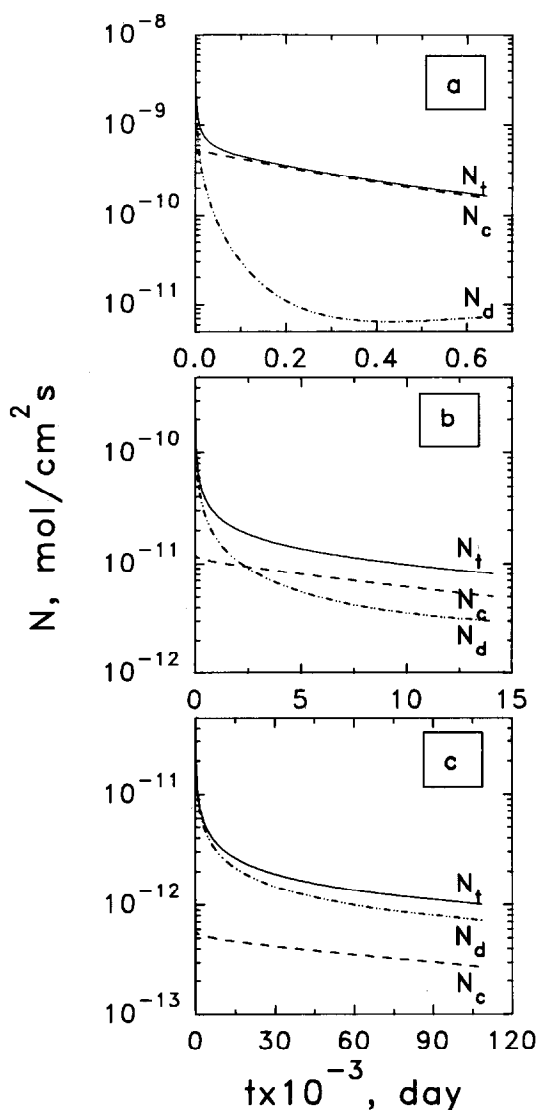


Fig. 3. Diffusion ( $N_d$ ), natural convection ( $N_c$ ) and total ( $N_t = N_d + N_c$ ) fluxes leaving the slab, as obtained from the simulation calculations: (a) benzene in tetradecane; (b) chlorobenzene in tetradecane; (c) 1,3-dichlorobenzene in tetradecane. For all three mixtures the initial concentration of the volatile compound is 0.1 mol fraction.

Finally, it is important to note that the total release time is also a strong function of the vapor pressure. At equal initial concentrations (0.1 molar fraction), the complete release of 1,3-dichlorobenzene requires a time which is about 170 times longer than that required to release benzene completely.



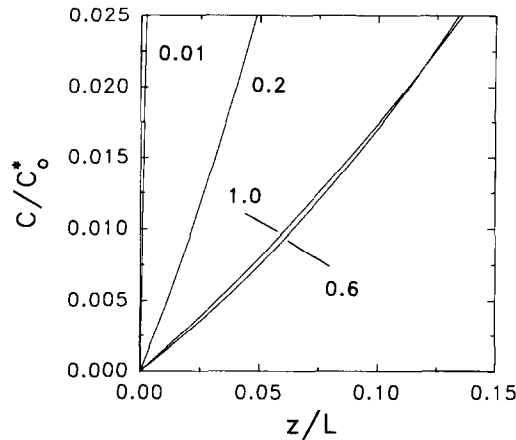


Fig. 4. Enlargement of Fig. 2(a) around the origin.

## 6. Conclusions

The results reported in Part I, regarding the release from single particles were extended to the analysis of a system of closer interest to environmental studies: the release of volatile toxic compounds from a slab of contaminated porous particles. Possible scenarios to which the model could apply are piles laying on the ground, or vented landfills. In the paper the attention is focused on the case that the particles forming the slab are imbued with an immobile oily liquid contaminated with a single volatile component. The modeling has accounted for both diffusive and free convection fluxes. The free convection is a mechanism that is usually disregarded in published models. We have shown that this mechanism plays an important role indeed. In particular, for volatile components having a vapor pressure of the order of that of benzene, the free convection predominates the overall release process.

## Nomenclature

- $a$  see Eq. (26)
- $a_v$  specific interparticle area, 1/cm
- $Bi$  Biot number referred to the single particle, see Eq. (1)
- $Bi_{ex}$  Biot number referred to the atmosphere/soil interface
- $C$  volatile gas-phase concentration in the interparticle porosity, mol/ml
- $C_i^*$  volatile gas-phase concentration in equilibrium with the liquid phase at the gas/particle interface, mol/ml
- $C_0^*$  volatile gas-phase concentration in equilibrium with initial liquid concentration  $c_0$ , mol/ml
- $c$  liquid-phase concentration of the volatile in the particles, mol/ml
- $c_0$  initial liquid-phase concentration of the volatile in the particles, mol/ml

$c_t$	total liquid-phase concentration, mol/ml
$d$	characteristic horizontal extension of the pile, m
$D_a$	free diffusivity of volatile component in air, $\text{cm}^2/\text{s}$
$D_s$	free diffusivity of volatile component in the solvent, $\text{cm}^2/\text{s}$
$D_p$	gas-phase effective diffusivity in the pile, see Eq. (5), $\text{cm}^2/\text{s}$
$D_{pa}$	gas-phase effective diffusivity in the dried-out zone, $\text{cm}^2/\text{s}$
$D_{pb}$	gas-phase effective diffusivity in the contaminated zone, $\text{cm}^2/\text{s}$
$f$	friction factor in the pile, see Eq. (36)
$g$	gravity, $\text{cm}/\text{s}^2$
$k$	permeability of the pile, see Eq. (37), $\text{cm}^2$
$K_g$	mass transfer coefficient based on gas-phase concentration, $\text{cm}/\text{s}$
$K_m$	mass transfer coefficient based on liquid-phase concentration, $\text{cm}/\text{s}$
$K_{ex}$	gas-phase external mass transfer coefficient, see Eq. (43), $\text{cm}/\text{s}$
$L$	pile height, cm
$L_c$	see Eq. (41), cm
$M$	molecular weight of volatile compound, g/mol
$M_a$	molecular weight of air, g/mol
$N_c$	convective flux leaving the pile from the bottom, based on the total cross-sectional area, $\text{mol}/\text{cm}^2 \text{ s}$
$N_d$	diffusive flux leaving the pile from the top, based on the total cross-sectional area, $\text{mol}/\text{cm}^2 \text{ s}$
NTU	number of transport units, see Eq. (6)
$Pe$	Peclet number, see Eq. (16)
$p^v$	vapor pressure of volatile compound, bar
$\Delta P_f$	friction loss in the pile, see Eq. (38), $\text{dynes}/\text{cm}^2$
$Q$	generation group, see Eq. (17)
$q$	intraparticle tortuosity factor
$q_p$	interparticle tortuosity factor
$\mathfrak{R}$	gas constant, $\mathfrak{R} = 83.14 \text{ bar ml}/\text{mol K}$
$R$	radius of the particle, cm
$Sc$	Schmidt number for the volatile compound, $Sc = \mu/(\rho_a D_a)$
$Sh$	Sherwood number, $Sh = 2RK_g q_p/D_a$
$T$	temperature, K
$t$	time, s
$t_f$	time necessary to reach $\lambda_f$ , s
$t_i$	time necessary to reach $\lambda_i$ , s
$u$	superficial velocity in the pile due to free convection, based on the total pile cross-sectional area, $\text{cm}/\text{s}$
$v_x$	wind speed at 10 m, $\text{m}/\text{s}$
$z$	distance in the vertical direction, cm

#### Greek symbols

$\Gamma$	dimensionless concentration, see Eq. (19)
$\varepsilon$	intraparticle porosity

$\varepsilon_p$	interparticle porosity
$\zeta$	dimensionless distance in the vertical direction, see Eq. (18)
$\lambda$	moving boundary position from the top of the slab, cm
$\lambda_i$	upper position of the boundary for the validity of the model, see Eq. (33), cm
$\lambda_r$	lower position of the boundary for the validity of the model, cm
$\mu$	viscosity of air, g/cm s
$\rho$	density of gas phase in the interparticle porosity, g/ml
$\rho_a$	density of air, g/ml
$\tau$	dimensionless release time ( $= t/t_r$ )

### Acknowledgements

This work was financed by research grants from “Ministero dell’Università e della Ricerca Scientifica e Tecnologica” and from “Consiglio Nazionale delle Ricerche”.

### Appendix

The exact solutions of Eqs. (20) and (21) with boundary conditions (22)–(25) are, respectively,

$$\Gamma = C_1 + C_2 \exp(Pe \zeta) \quad \text{for } \zeta < 0, \quad (\text{A.1})$$

$$\Gamma = C_3 \exp\left(\frac{Pe \times (1 + a)\zeta}{2}\right) + C_4 \exp\left(\frac{Pe \times (1 - a)\zeta}{2}\right) \quad \text{for } 0 < \zeta < 1, \quad (\text{A.2})$$

where  $Pe$  and  $a$  are defined in the Eqs. (16) and (26), respectively, and the constants  $C_1$ – $C_4$  can be obtained solving the following set of equations:

$$\begin{aligned} C_1 + C_2 \exp\left(-\frac{Pe \times \lambda}{L - \lambda}\right) &= 1, \\ C_2 - C_3 \frac{1 + a}{2} - C_4 \frac{1 - a}{2} &= 0, \\ C_1 + C_2 - C_3 - C_4 &= 0, \\ C_3(1 + a) \exp\left(\frac{Pe \times (1 + a)}{2}\right) + C_4(1 - a) \exp\left(\frac{Pe \times (1 - a)}{2}\right) &= 0. \end{aligned} \quad (\text{A.3})$$

For the case of major interest for which it is  $a \gg 1$ , the set of equations (A.3) reduces to:

$$\begin{aligned} C_1 &= C_4 \frac{a}{2} (1 - \exp(-Pe \times a)), \\ C_2 &= (1 - C_1) \exp\left(\frac{Pe \times \lambda}{L - \lambda}\right), \end{aligned} \quad (\text{A.4})$$

$$C_3 = C_4 \exp(-Pe \times a),$$

$$C_4 = \frac{\exp\left(\frac{Pe \times \lambda}{L - \lambda}\right)}{(1 + \exp(-Pe \times a)) - \frac{a}{2}(1 - \exp(-Pe \times a))\left(1 - \exp\left(\frac{Pe \times \lambda}{L - \lambda}\right)\right)}.$$

## References

- [1] L.J. Thibodeaux, *Chemodynamics. Environmental Movement of Chemicals in Air, Water and Soil*, Wiley, New York, NY, 1979.
- [2] L.J. Thibodeaux, K.T. Valsaraj, C. Springer and G. Hildebrand, Mathematical models for predicting chemical vapor emission from landfills, *J. Hazard. Mater.*, 19 (1988) 119–123.
- [3] A.A. Karimi, W.J. Farmer and M.M. Cliath, Vapor-phase diffusion of benzene in soil, *J. Environ. Qual.*, 16 (1987) 38–43.
- [4] A. Karimi, V. Ravindran and M. Pirbazari, A laboratory experiment and predictive model for evaluating landfill cover controls of emissions of volatile organic chemicals to air, *Haz. Waste Haz. Mater.*, 5 (1988) 203–218.
- [5] L.J. Thibodeaux and S.T. Hwang, Landfarming of petroleum wastes-modeling the air emission problem, *Environ. Prog.*, 1 (1982) 42–46.
- [6] R.R. Dupont, Evaluation of air emission release rate model predictions of hazardous organics from land treatment facilities, *Environ. Progr.*, 5 (1986) 197–206.
- [7] F. Gioia, F. Murena, G. Savino and P. Saha, The release into the atmosphere of hazardous volatiles: Part I. Release from porous solids imbued with a liquid mixture in which the volatiles are dissolved, *J. Hazard. Mater.*, 40 (1995) 213–235.
- [8] K.B. Bischoff, Accuracy of the pseudo steady state approximation for moving boundary diffusion problems, *Chem. Eng. Sci.*, 18 (1963) 711–713.
- [9] J.F. Wehner and R.H. Wilhelm, Boundary conditions of flow reactors, *Chem. Eng. Sci.*, 6 (1956) 89–93.
- [10] D. Mackay and R.S. Matsugu, Evaporation rates of liquid hydrocarbon spills on land and water, *Can. J. Chem. Eng.*, 51 (1973) 434–439.
- [11] R.B. Bird, W.E. Stewart and E.N. Lightfoot, *Transport Phenomena*, Wiley, New York, 1960, p. 199.
- [12] A.M.F.R. Pinto and J.R.F. Guedes de Carvalho, Transverse dispersion in granular beds. Part III. Mass transfer around particles dispersed in granular beds of inerts and the combustion of carbon particles in beds of sand, *Trans. Inst. Chem. Eng.*, 68, part A (1990) 503–509.