

Chemical volatilization from the soil matrix: Transport through the air and water phases

Jordi Grifoll^a, Yoram Cohen^{b,*}

^a*Escola Superior D'Enginyeria, University Rovira i Virgili, Tarragona, Catalonia, Spain*

^b*Department of Chemical Engineering, University of California, Los Angeles, CA 90024, USA*

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Abstract

A convenient theoretical approach is presented for the estimation of the fraction of a chemical volatilization flux from the soil matrix which is attributable to the various soil phases. Specifically, for a soil matrix consisting of soil–air, soil–water, and soil–solids, a volatilization index is defined which relates the contribution of these soil phases to the chemical volatilization flux from the soil. For the special case of local equilibrium among the soil phases and where diffusive transport dominates the volatilization index is shown to be a function of the chemical molecular diffusion coefficients in air and water, the Henry's law constant and the soil–water saturation. The application of the volatilization index is demonstrated, for the above limiting case, using basic physicochemical parameters for a number of different compounds.

1. Introduction

The problem of contaminant volatilization from the soil environment has received considerable attention in the literature. Numerous models which describe chemical volatilization from both nearly dry and partially saturated soils have been proposed [1–4]. Recent models of contaminant volatilization include the studies of Mayer et al. [3], Jury et al. [5–7], Corwin [8], Cohen et al. [9] and Cohen and Ryan [10]. The studies of Jury et al. [5–7] and Cohen and Ryan [10], in particular have addressed the issue of moisture movement in the soil and the resulting effect on contaminant volatilization. While early models of volatilization have provided a detailed account of the various transport and transformation processes which occur within the soil matrix, these models have been generally restricted to a 'pseudo-single phase' treatment of the soil matrix in the vadose zone. Although multiphase treatment of

* Corresponding author.

contaminant transport in the soil matrix has been described in a number of recent studies [10–12], it is not always immediately clear if a multiphase treatment is needed and whether the simple ‘pseudo-single phase’ treatment of contaminant transport in the soil would suffice.

Detailed models of contaminant transport in the vadose zone include processes such as diffusion, dispersion and convection phenomena for each of the phases present in the soil. Obviously, such models include a large number of parameters which depend on the chemical as well as soil properties. Often the necessary soil-specific parameters are not available or are not known to the same degree of accuracy as the basic physicochemical parameters of the chemical of concern (e.g., Henry’s law, aqueous solubility, molecular diffusivity in water and air). Therefore, in most volatilization estimates, predictive models are simplified to neglect the convective and, as a consequence, dispersive phenomena, not because they are insignificant but since their incorporation introduces a high level of complexity. Specifically, the movement of water and air in the vadose zone depends on diurnal temperature changes, precipitation events and evapotranspiration; thus, the coupling of moisture and temperature gradients to chemical transport in the vadose zone leads to a complex weather-dependent nature of chemical volatilization.

Clearly, the first task in establishing the level of required complexity in the analysis of volatilization is to determine if one needs to consider transport through both the soil–air and soil–water, simultaneously, or whether transport through only one of these phases (i.e. air or water) is sufficient. The objective of this paper is to provide a simple approach to elucidate the relative significance of transport through the soil–air and soil–water phases via a screening-level transport analysis. The approach introduces a *volatilization index* which is a measure of the fraction of the total volatilization flux which takes place via the soil–air and soil–water pathways.

2. The volatilization index

In the present analysis we focus on the one-dimensional chemical transport through the various soil phases of the soil vadose. The one-dimensional mass transfer equation can be described by the following set of unsteady convection–diffusion mass balance equations [10],

$$\frac{\partial \theta_i C_i}{\partial t} = \frac{\partial}{\partial z} \left[\theta_i \left(\frac{D_i}{\tau_i} + D_{v_i} \right) \frac{\partial C_i}{\partial z} \right] - \frac{\partial}{\partial z} (\theta_i V_i C_i) + \sum_{j=1, j \neq i}^M a_{ij} N_{ij} + R_i, \quad i = 1, \dots, M \quad (1)$$

in which z is the depth (m), C_i is the chemical concentration in phase i (e.g., mg/m³), the interstitial velocity of phase i is denoted by V_i (e.g., m/s), the volume fraction of phase i in the soil matrix is designated by θ_i , N_{ij} is the chemical mass flux from phase j to i (e.g., mg/m² s), a_{ij} is the interfacial area per unit volume of soil matrix, between phases i and j , and M is the total number of soil phases. The chemical molecular diffusion and convective dispersion coefficients in phase i are denoted by D_i and D_{v_i} ,

respectively, and the tortuosity of phase i is given by τ_i . Finally, the rate of chemical or biochemical transformations in phase i is given by R_i where production of the chemical occurs when $R_i > 0$ and degradation occurs when $R_i < 0$.

The volatilization flux at the soil/atmosphere interface is given by the following boundary condition [10]

$$\theta_i V_i C_i - \left(\theta_i \frac{D_i}{\tau_i} \right) \frac{\partial C_i}{\partial z} - \theta_i D_{vi} \frac{\partial C_i}{\partial z} = N_i, \quad i = 1, \dots, M, \quad z = 0 \quad (2)$$

which represents the equality of the mass flux at the interface from both the soil and the atmospheric sides of the interface, and where N_i is the surface volatilization flux attributed to phase i given by

$$N_i = \alpha_i k_{\text{atm}} (C_{\text{atm}} - C_a^*) + \beta_i \theta_i V_i C_i^*, \quad i = 1, \dots, M, \quad z = 0 \quad (3)$$

where C_a^* and C_i^* are the chemical concentrations in the soil–air phase and in soil phase i at the soil/atmosphere interface, respectively, and C_{atm} is the atmospheric bulk concentration. The first term on the right-hand side of Eq. (3) represents the mass flux (viewed from the atmospheric side of the soil/atmosphere interface) due to molecular and turbulent diffusion where k_{atm} denotes the atmospheric-side mass transfer coefficient. The coefficient α_i is the fractional contribution of soil phase i to the portion of the volatilization flux (at the atmospheric side of the soil/atmosphere interface) which is due to molecular and turbulent diffusion to the bulk atmosphere (at the edge of the atmospheric boundary layer, above the soil surface, where the concentration is given as C_{atm}) such that [10]

$$\sum_{i=1}^M \alpha_i = 1 \quad (4)$$

The second term on the right-hand side of Eq. (3) represents the convective chemical flux, at the atmospheric side of the soil/atmosphere interface, where the chemical is transported in the vertical direction away from the soil surface by air moving at a velocity V_a . The coefficient β_i represents the fraction of the chemical convective flux, at the atmosphere side of the soil/atmosphere interface, which is due to convective transport (see the Appendix). It is also instructive to note that the first, second and third terms on the left-hand side of Eq. (2) represent the contribution of convection, molecular diffusion and dispersion, respectively, to the chemical volatilization flux through the given phase.

The total chemical flux (i.e. $\sum N_i^0$), neglecting the special case of contaminant input via precipitation scavenging, can be obtained by summing Eq. (2) over the M soil phases to obtain

$$\sum_{i=1}^M \left[\theta_i V_i C_i - \theta_i \left(\frac{D_i}{\tau_i} + D_{vi} \right) \frac{\partial C_i}{\partial z} \right] = k_{\text{atm}} (C_{\text{atm}} - C_a^*) + \beta_a \theta_a V_a C_a^*, \quad z = 0 \quad (5)$$

where in deriving Eq. (5) it was assumed that convective transport across the soil/atmosphere interface (i.e. at the atmospheric side of the interface) occurs only via vapor phase transport which is represented by the term $\beta_a \theta_a V_a C_a^*$ in which the

subscript denotes the air phase. The chemical which is transported to the soil/atmosphere interface is subsequently transported from the atmospheric side of the soil/air interface into the atmospheric boundary layer both by convective motion (i.e. due to a vertical velocity of the air phase which is injected into the atmosphere from the soil phase) and by diffusional transport which is governed by a concentration driving force (see Appendix A). When the convective chemical transport is from the soil to the atmosphere the vertical convective velocity V_a decreases as one moves away from the surface into the atmospheric boundary layer above the soil surface. Therefore, only a fraction of the chemical which is transported across the interface by convection is transported across the atmospheric boundary layer. The fraction of the chemical convective flux which is transported away from the soil surface and across the atmospheric boundary layer (above the soil surface) via convection is denoted by β_a with the remainder being transported by molecular and turbulent diffusion. When convective interfacial transport of the chemical is from the soil to the atmosphere the value of β_a can be estimated via a simple mass transfer analysis as illustrated in the Appendix.

The fractional contribution of any one of the soil phases to the diffusional flux, denoted here by α_i , can be obtained from the combination of Eqs. (2)–(5). Accordingly, α_i is given by

$$\alpha_i = \frac{(1 - \beta_i)\theta_i V_i C_i - \theta_i \left(\frac{D_i}{\tau_i} + D_{V_i} \right) \frac{\partial C_i}{\partial z}}{\sum_{j=1}^{M-1} \left[(1 - \beta_j)\theta_j V_j C_j - \theta_j \left(\frac{D_j}{\tau_j} + D_{V_j} \right) \frac{\partial C_j}{\partial z} \right]}, \quad i = 1, \dots, M - 1, \quad z = 0 \quad (6)$$

It is important to note that convection and dispersion is not a feasible transport mechanism for chemical transport along the soil–solids phase. Also, the solid phase diffusion (e.g., surface diffusion along the solid phase) is at least several orders of magnitude smaller than diffusion in the mobil soil phases. Therefore, it is appropriate to assume that the soil–solids phase is not a pathway for volatilization. Nonetheless, the soil–solids phase does reduce the rate of volatilization due to solute sorption. It must be noted, however, that the soil–solids phase does not affect the relative proportions of the volatilization flux that are accommodated by the soil–fluid phases. Hence, in writing Eq. (6) for the relative volatilization fluxes the soil–solids phase can be omitted from the summation which is carried out over $M - 1$ of the soil phases.

Although Eq. (6) is of general validity, in order to compute α_i , the concentrations, concentration gradients and phase velocities (of the soil–air and soil–water) at $z = 0$ must be known. We note, however, that for the special case when the assumption of interfacial chemical equilibrium is invoked, Eq. (6), which is applicable at the soil/atmosphere interface, can be expressed as

$$\alpha_i = \frac{(1 - \beta_i)\theta_i V_i C_i - \theta_i \left(\frac{D_i}{\tau_i} + D_{V_i} \right) \frac{\partial C_i}{\partial z}}{\sum_{j=1}^{M-1} \left[(1 - \beta_j)\theta_j V_j \frac{C_i}{H_{ij}} - \frac{\theta_j}{H_{ij}} \left(\frac{D_j}{\tau_j} + D_{V_j} \right) \frac{\partial C_i}{\partial z} \right]}, \quad i = 1, \dots, M - 1, \quad z = 0 \quad (7)$$

in which H_{ij} are the soil phase i /phase j chemical partition coefficient (i.e. $H_{ij} = C_i/C_j$). A further simplification of Eq. (7) results when convection and hence dispersion effects are negligible. In this limiting case the fractional contribution of phase i to the total flux can be written as

$$\alpha_i = \frac{\theta_i(D_i/\tau_i)}{\sum_{j=1}^{M-1} \left[\frac{1}{H_{ij}} \left(\theta_j \frac{D_j}{\tau_j} \right) \right]}, \quad i = 1, \dots, M-1, \quad z = 0 \quad (8)$$

It is interesting to note that Eq. (8) is independent of the concentration field and can be used for a first-order analysis to elucidate the relative importance of the soil phases for chemical transport. Also, when a numerical solution of Eq. (1) is sought, the expression for α_i as given by Eq. (8) provides a first-order estimate which is needed when applying the boundary conditions (i.e. Eqs. (3) and (5)).

In the special case when chemical equilibrium is also assumed to exist among the bulk soil phases (in addition to the interface) for a soil matrix consisting of soil-air, soil-water, and soil-solids phases, and in the absence of convective and dispersive transport, the set of equations described by Eq. (1) can be rearranged and expressed in terms of the soil matrix concentration to yield

$$\frac{\partial C_{sm}}{\partial t} = \frac{\partial}{\partial z} \left[\left(\theta_a \frac{D_a}{\tau_a} + \frac{\theta_w}{H_{aw}} \frac{D_w}{\tau_w} \right) \frac{\partial(C_{sm}/\xi)}{\partial z} \right] + R \quad (9)$$

where C_{sm} is the total chemical concentration in the soil matrix (e.g., mg/m³ soil) defined as

$$C_{sm} = \sum_{j=1}^3 \theta_j C_j \quad (10)$$

in which the subscripts $j = 1, 2, 3$ denote the soil-air, soil-water, and soil-solids phases, respectively, and

$$\xi = \frac{\theta_s}{H_{as}} + \theta_a + \frac{\theta_w}{H_{aw}} \quad (11)$$

Finally, the overall rate of chemical or biochemical transformations is given by R . From Eq. (9) it is apparent that the contribution of the air and water phases to the diffusional transport is proportional to $\theta_a D_a/\tau_a$ and $H_{wa}\theta_w D_w/\tau_w$, respectively. Thus, the expression for α_i as given in Eq. (8) is applicable within the soil matrix as well as at the soil/atmosphere interface.

When diffusional transport dominates (i.e. convective transport is negligible), as denoted in Eq. (8), it is possible to construct a simple approach to determine the fraction of the total volatilization flux due to the various phases of the soil matrix. For a soil that consists of the soil-solids, soil-air and soil-water phases, the expression for the fraction of the total flux attributed to transport in the soil-air, α_a (Eq. (8)), can be

written as

$$\alpha_a = \frac{\frac{\theta_a D_a}{\tau_a}}{\frac{\theta_a D_a}{\tau_a} + \frac{\theta_w D_w}{\tau_w H_{aw}}} = \frac{1}{1 + q \frac{\theta_w \tau_a}{\theta_a \tau_w}} \quad (12)$$

where q is a chemical-specific parameter defined by

$$q = \frac{1}{H_{aw}} \left(\frac{D_w}{D_a} \right) \quad (13)$$

whereas the remainder of the terms in Eq. (12) are a function of the volumetric content and the tortuosity of phase i . However, since the tortuosity can be related to the volumetric phase content, Eq. (8) is only a function of q and the volume fraction of each phase. For a given soil, the total porosity can be expressed as

$$\varepsilon = \theta_a + \theta_w \quad (14)$$

and thus the required soil properties in Eq. (12) are the soil porosity and the soil moisture content expressed as volume fraction. If a specific model is chosen to evaluate the tortuosities then the evaluation of α_a is straightforward. For example, one of the popular models used to evaluate tortuosities of the soil phases is the Millington model [13] given by

$$\tau_i = \frac{\varepsilon^2}{\theta_i^{2.3}} \quad (15)$$

which is assumed to apply to both the soil-air and soil-fluid phases [10]. Subsequently, in order to generalize Eq. (12) to soils of different total porosity, the water-phase saturation, S_w , is introduced

$$S_w = \frac{\theta_w}{\varepsilon}, \quad (16)$$

leading to the expression of Eq. (12) as a function of q and S_w only

$$\alpha_a = \frac{1}{1 + q \left(\frac{S_w}{1 - S_w} \right)^{3.3}} \quad (17)$$

The parameter α_a , given by Eq. (17), represents the fraction of the total volatilization flux which is attributable to diffusion in the soil-air phase and it can be regarded as a volatilization index. The value of α_a ranges from a value of zero to unity. As the value of α_a approaches unity the chemical can be considered as a highly volatile chemical for the soil conditions under consideration. Conversely, for chemicals under soil conditions where the volatilization index is small (i.e. $\alpha_a \ll 1$) the chemical has little

propensity to volatilize from the soil matrix. From the view point of model application, for chemicals with a value of α_a near zero a model that focuses on transport in the soil-water is required while for chemicals with a value of α_a near unity one only needs to consider transport through the soil-air. In both cases chemical adsorption onto the soil solids is included in the analysis of the volatilization flux as is apparent from the presence of the soil-air chemical partition coefficient which is present in Eq. (9) through the term ξ (see Eq. (11)) and through the interfacial mass flux between the soil-fluid phase and soil-solids phase as indicated in Eq. (1).

Table 1
Values of D_a , D_w , H_{aw} and q for different chemicals

Compound	$D_a \times 10^5$ (m ² /s)	$D_w \times 10^9$ (m ² /s)	H_{aw}^a	q
1 Acrolein	1.1	1.1	1.8×10^{-4}	0.56
2 Benzene	0.88	0.90	0.22	4.6×10^{-4}
3 Benzo[b]fluoranthene	0.49	0.46	5.0×10^{-4}	0.19
4 Chlordane	0.43	0.30	2.0×10^{-3}	0.035
5 Chloroethane	1.05	1.1	0.35	3.0×10^{-4}
6 Chloroethene	1.1	1.1	2.3	4.3×10^{-5}
7 Chloroform	0.88	0.92	0.22	4.8×10^{-4}
8 Chloromethane	1.3	1.3	0.41	2.4×10^{-4}
9 2-Chloronaphthalene	0.64	0.60	0.025	3.8×10^{-3}
10 1,2-Dibromo-3-chloropropane	0.70	0.69	0.010	9.5×10^{-3}
11 1,1-Dichloroethane	0.89	0.91	0.24	4.3×10^{-4}
12 1,2-Dichloroethane	0.89	0.91	0.047	2.2×10^{-3}
13 Dichloromethane	1.0	1.1	0.10	1.1×10^{-3}
14 2,4-Dichlorophenol	0.69	0.67	1.3×10^{-4}	0.75
15 Heptachlor	0.45	0.32	0.096	7.4×10^{-4}
16 Hexachlorocyclohexane (Lindane)	0.52	0.42	3.9×10^{-4}	0.21
17 Methanol	1.6	1.5	1.9×10^{-4}	0.49
18 Methyl ethyl ketone	0.905	0.895	1.9×10^{-3}	0.052
19 Methyl isobutyl ketone	0.74	0.69	6.1×10^{-4}	0.15
20 Pentachlorophenol	0.58	0.495	8.0×10^{-5}	1.1
21 Pyrene	0.57	0.605	6.2×10^{-4}	0.17
22 2,3,7,8-Tetrachloro dibenzo- <i>p</i> -dioxin	0.51	0.36	6.7×10^{-4}	0.105
23 Tetrachloroethylene	0.74	0.74	0.43	2.3×10^{-4}
24 Toluene	0.79	0.78	0.28	3.5×10^{-4}
25 Toxaphene	0.43	0.25	2.6	2.2×10^{-5}
26 1,1,1-Trichloroethane	0.79	0.80	0.62	1.6×10^{-4}
27 Trichloroethylene	0.81	0.835	0.41	2.5×10^{-4}
28 Trichloromethane	0.88	0.92	0.22	4.8×10^{-4}
29 Xylene	0.73	0.69	0.26	3.7×10^{-4}

^a Values of the Henry's law constant were taken to be the values nearest to 20°C. When the temperature was not reported and various values were given, the value of the Henry's law constant reported in the table is the average of the reported values.

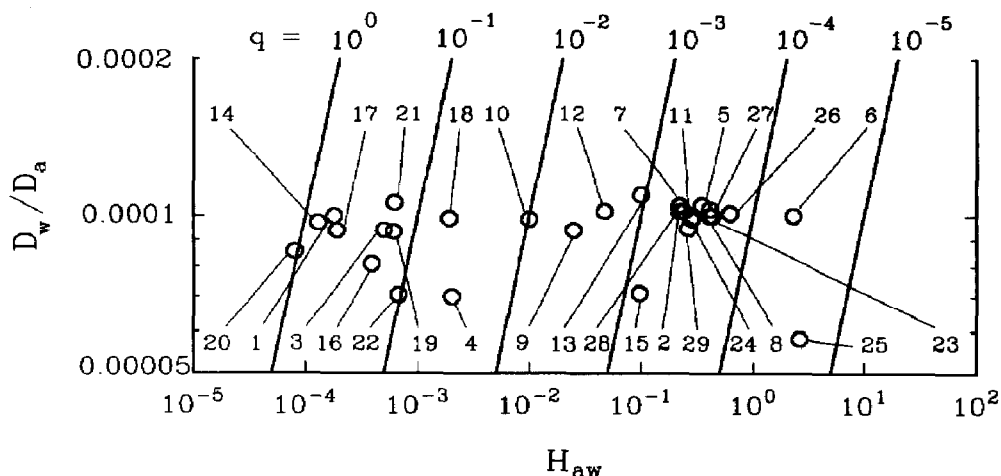


Fig. 1. Values of q as a function of the molecular mass diffusivities in water and air and the dimensionless Henry's law constant. The numbers in the figure correspond to the chemicals listed in Table 1.

3. Discussion

In order to illustrate the application of the volatility index as expressed in Eq. (17) (under the condition of diffusion dominated transport) values of q , corresponding to the chemical-specific values of H_{wa} , D_a , D_w , were calculated for a number of different chemicals and the results are given in Table 1. In the absence of experimental values of the molecular diffusivities the correlations of Fuller et al. [14] and Hayduk and Minhas [15] were utilized to calculate the molecular diffusivity in the air and water phases, respectively. The values of H_{aw} (the dimensionless Henry's law constant) were taken mainly from the compilations of Montgomery and Welkom [16,17] and Howard [18]. As indicated in Table 1 the Henry's law constant for the listed chemicals varies by four orders of magnitude. In contrast, the ratio D_w/D_a appears to be a nearly chemical-independent constant with a value of about 10^{-4} for the chemicals listed in Table 1. Fig. 1 provides a graphical illustration of the dependence of q on the diffusivity ratio D_w/D_a and the Henry's law constant H_{aw} . It is clear from Fig. 1 that the variability in the parameter q for the different chemicals is largely due to the variability in the Henry's law constant. In fact, it is interesting to note that, in the absence of molecular diffusivity information, a reasonable estimation of the value of q could be obtained by simply assuming that the ratio D_w/D_a equals about 10^{-4} .

The dependence of the volatility index, α_a , as calculated from Eq. (15) is shown in two alternative plots depicted in Figs. 2a and 2b for values of q ranging from about 10 to 10^{-6} . Since q represents the chemical's tendency to diffuse through the soil-water phase, as depicted in Fig. 2a, for a given value of the soil saturation, higher values of q result in a smaller fraction of the total volatilization flux being supported by the soil-air phase. Also, for a given chemical (i.e. for a given value of q), as the soil-water saturation increases the fraction of the total volatilization flux attributable to diffusion through the air-phase decreases rapidly as depicted in Fig. 2b. For example, for

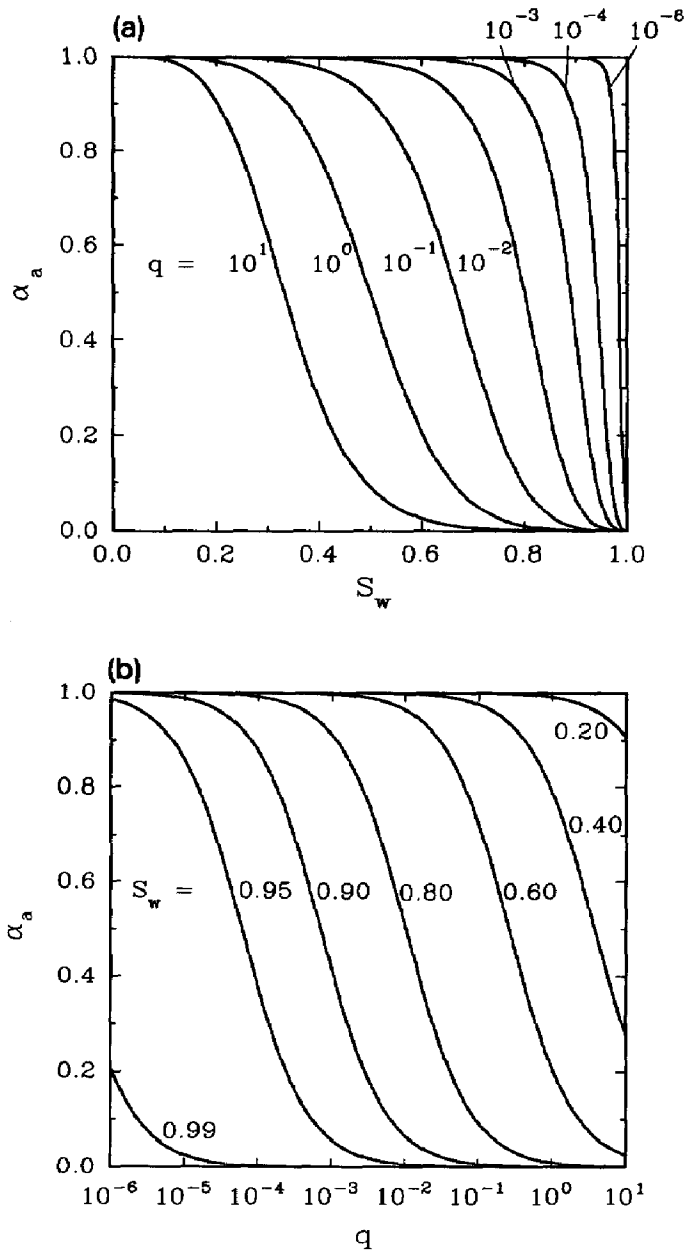


Fig. 2. (a) Variation of the volatilization index with q for different soil-water saturations. (b) Variation of the volatilization index with soil-water saturation for different q values.

$q = 10$ at water saturations of 0.33 and 0.7 about 50% and 0.6%, respectively, of the total chemical transport takes place in the air phase, whereas for $q = 10^{-6}$ even with water saturation values of up to 0.94, nearly 99% of the volatilization flux is due to transport in the soil-air phase. Thus, for the above example, for the low q value (i.e. $q = 10^{-6}$) only transport through the soil-air needs to be considered. On the other hand, for large q values and at low water saturation values, chemical diffusion through both the air and water phases of the soil must be considered.

The above illustration is strictly valid for the case where chemical volatilization is dominated by diffusive transport. Under conditions where convective transport is important (e.g., when moisture and/or temperature gradients in the top soil region are significant) the volatilization flux should be determined using Eqs. (6) or (7). Generally, convective effects will be of significance if the condition $Pec_i \gg 1$ holds, where Pec_i is the Péclet number (for either the soil–water or soil–air phases) defined as $Pec_i = V_i L / D_i$ in which L is the depth of the top soil zone.

4. Conclusions

When a chemical diffuses through the unsaturated soil zone, the volatilization index, as given by Eq. (17) for the case of diffusion-dominated transport, provides a simple way to evaluate the relative contribution of the air phase to total diffusive transport through the soil matrix. The volatilization index is a function of the soil water saturation and the chemical parameter q which, in the absence of molecular diffusivity data, can be estimated as being equal to approximately $1/(10000 H_{aw})$. When the value of the volatilization index is near unity air transport dominates and as the volatilization index approaches zero water phase transport dominates. Intermediate values of the volatilization index suggest the use of a multiphase description of transport through the soil matrix. Moreover, the error in the calculated volatilization flux, resulting from neglecting either the air or water phases, can be estimated from the volatilization index. When convective transport effects become significant then Eqs. (6) or (7) should be used to determine the volatilization index. Finally, for a multiphase description of contaminant volatilization from the soil matrix the appropriate flux boundary conditions, for each of the soil phases, are given by Eq. (3). The volatilization index, α_i can be calculated a priori only for the limiting case of local equilibrium and when diffusive transport is the dominant mode of chemical transport. For the more general case, α_i is not known a priori and must be determined by an iterative calculation as part of the overall solution of the convective–diffusion equations for the separate soil phases.

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Appendix

The transport of chemicals in the soil matrix towards the soil/atmosphere interface is due to both convective and diffusional transport mechanisms. Similarly, from the

atmosphere side of the soil/atmosphere interface chemical transport across the turbulent atmospheric boundary layer above the soil surface occurs by both convective transport and diffusional transport (both molecular and turbulent). Only a portion of the chemical that crosses the soil/atmosphere interface due to convective motion is carried across the atmospheric boundary layer by convection. An exact analysis of the above transport process is only possible using the microscopic equations for momentum and mass transfer above the soil, considering the exact shape of the interface and a complete description of the prevailing meteorological conditions (wind velocity profile, temperature, humidity, etc.). However, an approximate analysis for estimating the value of β_a as defined in Eq. (5) is possible as described in the example below.

Chemical mass transfer across the atmospheric boundary layer (above the soil surface) can be analyzed by a variety of turbulent mass transfer models. For example, Brutsaert [19] analyzed the problem of interfacial mass transfer by considering an interfacial sublayer of depth h , near the soil surface, and a dynamic sublayer where the velocity and logarithmic velocity profiles are assumed to exist. Once the solute reaches the soil surface, its transport from the soil/atmosphere interface across the interfacial layer (but not the dynamic layer) can be described by the following relation:

$$N_i^0 = k_0(C_h - C_a^*) + \theta_a V_a C_a^* \quad (\text{A.1})$$

in which C_h is the chemical concentration (in the atmosphere) at the edge of the interfacial sublayer, located at distance h above the soil surface, C_a^* is the concentration in the air phase at the soil/atmosphere interface and k_0 is the interfacial sublayer mass transfer coefficient that can be estimated from [19]:

$$k_0 = \frac{u_*}{7.3 \text{Re}_0^{1/4} \text{Sc}^{1/2}} \quad (\text{A.2})$$

in which $\text{Re}_0 = u_* z_0 / \nu$ is the roughness Reynolds number, $\text{Sc} = \nu / D_a$ is the Schmidt number, u_* is the atmosphere-side friction velocity, z_0 the characteristic roughness length of the soil surface and ν the kinematic viscosity of the air.

The chemical flux that crosses the dynamic sublayer (located above the interfacial sublayer) is given by [19]

$$N = k_1(C_{\text{atm}} - C_h) \quad (\text{A.3})$$

where k_1 , the mass transfer coefficient for the dynamic sublayer, is given by

$$k_1 = \frac{u_*^2}{\text{Sc}_t(U_{\text{atm}} - U_h)} \quad (\text{A.4})$$

where U_{atm} and C_{atm} are the air velocity and concentration (at the upper edge of the dynamic sublayer) at a reference height, z_r , U_h is the air velocity at the edge of the interfacial sublayer and Sc_t the turbulent Schmidt number. The variables appearing in Eq. (A.4) can be estimated [19] as $\text{Sc}_t = 1$, $U_h/u_* = 5$ and u_* can be estimated from the wind velocity profile. For example, for a neutral atmospheric stability condition the

usual logarithmic velocity profile can be used

$$\frac{U_{\text{atm}}}{u_*} = \frac{1}{\kappa} \ln \left(\frac{z_r}{z_0} \right) \quad (\text{A.5})$$

where $\kappa = 0.4$ is the von Karman constant.

After eliminating C_h between Eqs. (A.2) and (A.3) the chemical flux at the soil surface can be expressed as

$$N_i^0 = \frac{k_1 k_0}{k_0 + k_1} (C_{\text{atm}} - C_a^*) + \frac{k_1}{k_0 + k_1} \theta_a V_a C_a^* \quad (\text{A.6})$$

and upon comparison of Eq. (A.3) to Eq. (A.6) one can deduce the following:

$$k_{\text{atm}} = \frac{k_1 k_0}{k_0 + k_1} \quad (\text{A.7})$$

and

$$\beta_a = \frac{k_1}{k_0 + k_1} \quad (\text{A.8})$$

Eq. (A.7) is the expression for the mass transfer coefficient obtained by Brutsaert [19] and Eq. (A.8) provides an estimate of the fraction of the soil–air convective flux that is transported convectively to the bulk atmosphere.

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