

# The effects of nonlinear sorption on the diffusion of volatile organic compounds from air-dry soils: A theoretical study

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## Abstract

The effects of nonlinear (Brunauer–Emmett–Teller, BET) sorption on the rates of diffusion of volatile organic compounds (VOCs) within and from uniformly contaminated air-dry soils were evaluated by numerical solution of the one-dimensional gas-phase diffusion equation. A dimensionless sorption parameter, which accounts for the importance of BET sorption on the diffusive transport, was identified. Numerical simulations demonstrated that the dimensionless gas-phase and total-soil concentration profiles, and the dimensionless emission rates of VOC from the soil surface, varied in response to changes in the initial concentration of the VOC in the soil, in marked contrast with the case of linear sorption of the VOC. The sensitivity of the numerical results towards the BET sorption parameters in the model was evaluated. A linearization step in the derivation of the continuity equation of diffusion and BET sorption was used to obtain an analytical solution for the soil surface flux of VOC to the atmosphere, by substituting a linear sorption isotherm for the BET isotherm. The errors associated with this step were evaluated and the deviations were found to be < 20% for all cases tested in comparison to the full numerical solutions.

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## 1. Introduction

Volatile organic compounds (VOCs) have been introduced into the soil from a number of sources, which include accidental spills on the soil surface, leaks from underground storage tanks and from surface impoundments, and from intentional burial at hazardous waste storage and disposal facilities. In many relevant situations in the environment, VOCs emanating from subsurface sources must traverse a soil surface layer which is air-dry before emitting into the atmosphere. In the case of

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air-dry soils, VOC sorption from the gas phase to solids is nonlinear and of the BET type [1–5]. The movement of these pollutants in the soil gas phase and transfer to the atmosphere are important issues in understanding the ultimate fate of these compounds in the environment. Mathematical models which accurately describe the rates of transfer from the bulk soil phase to the atmosphere are important tools in understanding and ultimately controlling air pollution originating from contaminated soils.

Essentially all of the models appearing in the literature that describe VOC transport in the soil vadose zone have assumed linear equilibrium sorption of organic contaminants to the soil solids from both the aqueous and gas phases [6–10]. Using the assumption of linear equilibrium sorption, analytical solutions are often available for the concentration profiles and emission rates from the soil to atmosphere. There have been models incorporating nonlinear sorption into the analysis of VOC diffusion from both saturated and nearly dry soils [11, 12]. However, studies of VOC diffusion and nonlinear sorption which specifically address the effects of nonlinear sorption on soil concentration profiles and emission rates have not previously appeared.

In this paper, the effects of nonlinear sorption on the gas-phase diffusion of VOCs within and from air-dry soils are evaluated utilizing the BET sorption parameters and soil physical properties measured in a separate paper [13]. Two soils, each significantly different in sorption capacity, and benzene as the model VOC, were used to provide input parameters for the numerical simulations. Benzene was chosen for this work because it is a common pollutant in contaminated soils and its sorption in air-dry soils has been extensively studied [1–3, 13, 14]. The assumptions leading to the diffusion and nonlinear sorption equation are discussed and the numerical method of solution is presented. In the course of the derivation of the diffusion equation, a dimensionless sorption parameter is defined which quantifies the importance of sorption to the diffusive transport of VOC in air-dry soils. In the limit of dilute soil contamination levels, an analytical solution to the diffusion and nonlinear sorption equation is presented for the emission flux of VOC. Numerical soil gas-phase and total-soil concentration profiles are generated along with emission rates of VOCs from soil to the atmosphere, and their dependence upon the degree of isotherm nonlinearity is evaluated. Finally, an approximate analytical solution to the equation of diffusion and nonlinear BET sorption, made possible by introducing an isotherm linearization step into the model development, is presented and evaluated for accuracy.

## 2. Theory

### 2.1. Diffusion and BET sorption in air-dry soil

It has been shown in recent reviews that chemical species which migrate through the soil gas phase to the atmosphere do so primarily by gas-phase diffusion [14, 15]. Convective mechanisms may dominate only under relatively short, transient periods. Therefore, in the following theoretical developments, only diffusive transport in the

soil gas phase is considered for air-dry soils. Reversible equilibrium partitioning between the soil solid and gas phases is modeled using the BET sorption isotherm. A one-dimensional and time-dependent diffusion process is considered with the only spatial dimension being the soil depth. Fick's first law governs the diffusive transport (dilute concentration of VOCs in the gas phase of the soil) and isothermal conditions are assumed. Since equilibrium sorption is assumed, no mass transfer limitations are considered between the soil gas phase and the sorbed phase.

Fig. 1 shows the multiphase system under consideration. The soil is assumed to be composed of a gas phase and a solid phase. The solid phase is composed of agglomerations of individual soil grains [14]. The soil grains themselves are taken to be essentially nonporous and the porosity of the soil agglomerations is assumed to be the same as the porosity of the bulk matrix.

The volume-averaged diffusion equation, describing the change in gas-phase concentration of the VOC in air-dry soil, is

$$\left( \varepsilon_v + \rho_B \frac{\partial U_A}{\partial C_g} \right) \frac{\partial C_g}{\partial t} = \varepsilon_v D_{\text{eff}} \frac{\partial^2 C_g}{\partial z^2}, \quad (1)$$

where  $C_g$  is the intrinsic volume-averaged gas-phase soil concentration of the VOC (g VOC/cm<sup>3</sup> gas),  $\rho_B$  is the soil bulk density (g soil solids/cm<sup>3</sup> soil),  $\varepsilon_v$  is the soil void fraction,  $U_A$  is the sorbed concentration of VOC (g VOC/g soil solids),  $t$  is time (s),  $z$  is soil depth (cm), and the effective diffusivity is obtained from the Millington-Quirk relationship,  $D_{\text{eff}} = D_{\text{AB}} \varepsilon_v^{1/3}$  (cm<sup>2</sup>/s) [16]. The intrinsic volume-averaged gas-phase soil concentration has been defined elsewhere [17].

The expression for the BET sorption isotherm used in Eq. (1) is listed in terms of  $C_g$  as [18]

$$U_A = b U_{\text{Am}} \frac{(C_g/C_{\text{AS}})[1 - (n+1)(C_g/C_{\text{AS}})^n + n(C_g/C_{\text{AS}})^{(n+1)}]}{(1 - C_g/C_{\text{AS}})[1 + (b-1)(C_g/C_{\text{AS}}) - b(C_g/C_{\text{AS}})^{(n+1)}]}, \quad (2)$$

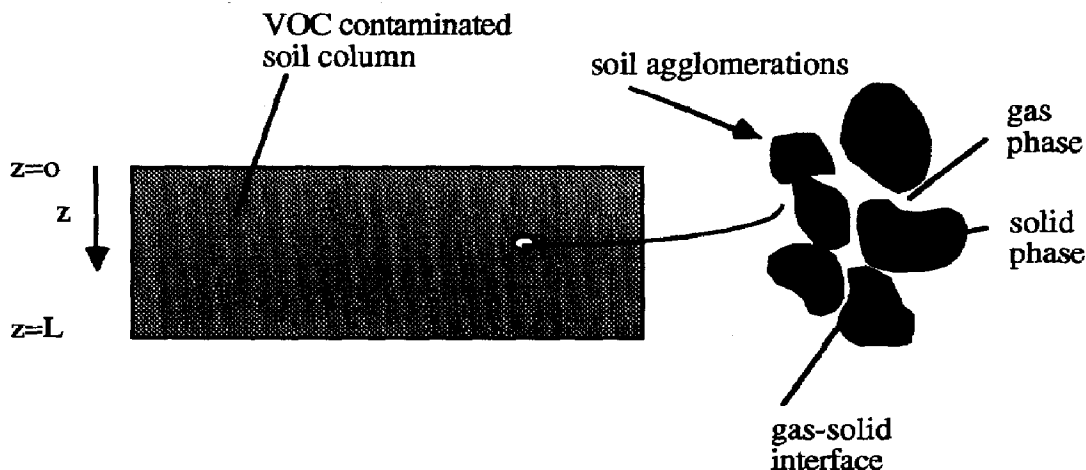


Fig. 1. Schematic diagram of a column of air-dry soil. Agglomerations of soil are composed of smaller individual soil particles.

where  $U_{Am}$  is the mass of sorbed VOC at monolayer coverage (g VOC/g soil solids),  $C_{AS}$  is the saturation vapor concentration of VOC (g VOC/cm<sup>3</sup> gas) at the temperature of interest  $T$ ,  $b$  is the BET energy parameter defined as  $b = \exp[(\Delta H_a - \Delta H_v)/RT]$ , where  $\Delta H_a$  and  $\Delta H_v$  are the enthalpies of sorption and vaporization, respectively (kcal/mol VOC),  $n$  is the maximum number of sorbed layers, and  $R$  is the ideal gas constant (kcal/(mol K)).

The initial and boundary conditions for the problem assume an initially uniform soil contamination level with the VOCs emitting into a clean atmosphere above the soil surface and an impermeable barrier at the base of the column of soil. These conditions are

$$t = 0, \quad 0 \leq z \leq L, \quad C_g = C_{g0}, \quad (3)$$

$$t > 0, \quad z = 0, \quad C_g = 0, \quad (4)$$

$$t > 0, \quad z = L, \quad \frac{\partial C_g}{\partial z} = 0, \quad (5)$$

where  $C_{g0}$  is the initial value of  $C_g$ , and  $L$  is the depth of the soil column (cm). The diffusion equation as stated in Eq. (1) and the initial and boundary conditions stated in Eqs. (3)–(5) are cast in dimensionless form. The dimensionless soil gas-phase concentration, the dimensionless time, and the dimensionless soil depth, respectively, are defined as

$$\Phi = \frac{C_g}{C_{g0}}, \quad \theta = \frac{tD_{eff}}{L^2}, \quad Z = \frac{z}{L}, \quad (6)$$

where  $L$  is the depth of the actual soil column. When these dimensionless quantities are substituted into Eqs. (1) and (3)–(5), the resulting dimensionless diffusion equation, boundary, and initial conditions are

$$\left(1 + \xi \frac{\partial(U_A/U_{Am})}{\partial \Phi}\right) \frac{\partial \Phi}{\partial \theta} = \frac{\partial^2 \Phi}{\partial Z^2}, \quad (7)$$

$$\theta = 0, \quad 0 < Z < 1, \quad \Phi = 1, \quad (8)$$

$$\theta > 0, \quad Z = 0, \quad \Phi = 0, \quad (9)$$

$$\theta > 0, \quad Z = 1, \quad \frac{\partial \Phi}{\partial Z} = 0, \quad (10)$$

where the dimensionless BET sorption isotherm is

$$\frac{U_A}{U_{Am}} = \frac{b\Phi\delta[1 - (n+1)(\Phi\delta)^n + n(\Phi\delta)^{(n+1)}]}{(1 - \Phi\delta)[1 + (b-1)\Phi\delta - b(\Phi\delta)^{(n+1)}]}. \quad (11)$$

In the dimensionless diffusion equation above (Eq. (7)) and the dimensionless BET sorption isotherm (Eq. (11)), two additional dimensionless quantities are defined, the

dimensionless sorption parameter,

$$\xi = \frac{\rho_B U_{Am}}{\varepsilon_y \delta C_{AS}}, \quad (12)$$

and the dimensionless initial gas-phase concentration of VOC in the soil,

$$\delta = \frac{C_{g0}}{C_{AS}}. \quad (13)$$

When the following relationship holds (from (17)),

$$1 + \xi \frac{\partial(U_A/U_{Am})}{\partial\Phi} \gg 1, \quad (14)$$

sorption of VOC to soils can significantly retard the movement of VOC within soils and the rates of emission from soil to the atmosphere.

Using a Crank–Nicolson finite difference numerical method, Eqs. (7)–(11) were solved on a DEC VAX780. Eq. (7) was discretized as

$$\left[ 1 + \xi \frac{\partial(U_A/U_{Am})}{\partial\Phi} \right]_i^{k+1/2} \left[ \frac{\partial\Phi}{\partial\theta} \right]_i^{k+1/2} = \frac{1}{2} \left[ \frac{\partial^2\Phi}{\partial Z^2} \right]_i^{k+1} + \frac{1}{2} \left[ \frac{\partial^2\Phi}{\partial Z^2} \right]_i^k. \quad (15)$$

A Richtmeyer linearization scheme was used on the nonlinear sorption term in Eq. (15):

$$\left[ \frac{\partial(U_A/U_{Am})}{\partial\Phi} \right]_i^{k+1/2} = \left[ \frac{\partial(U_A/U_{Am})}{\partial\Phi} \right]_i^k + \frac{\Delta\theta}{2} \left[ \frac{\partial}{\partial\theta} \left[ \frac{\partial(U_A/U_{Am})}{\partial\Phi} \right]_i^k \right]. \quad (16)$$

A clustering of numerical mesh points was generated at the soil surface ( $Z = 0$ ) by using the Robert's grid transform [19]. The accuracy of the numerical method was confirmed by comparing the analytical solution for diffusion and BET sorption in the limit of dilute VOC concentration. The analytical solution to the dilute limit problem is presented next.

## 2.2. Diffusion of VOC in the dilute limit of BET sorption

In the dilute limit, the BET equation (Eq. (2)) reduces to a more simple linear form:

$$U_A = U_{Am} b \frac{C_g}{C_{AS}}. \quad (17)$$

The continuity equation for diffusion and equilibrium sorption (Eq. (1)) then is

$$\left( \varepsilon_y + \rho_B b \frac{U_{Am}}{C_{AS}} \right) \frac{\partial C_g}{\partial t} = \varepsilon_y D_{\text{eff}} \frac{\partial^2 C_g}{\partial Z^2}. \quad (18)$$

Using the dimensionless quantities defined by Eq. (6), Eq. (18) becomes

$$(1 + b\xi) \frac{\partial\Phi}{\partial\theta} = \frac{\partial^2\Phi}{\partial Z^2} \quad (19)$$

and the solution to Eq. (19) for the magnitude of the dimensionless flux of VOC from the soil to the atmosphere, valid at short times in the diffusion process, is [20]

$$\frac{\partial \Phi}{\partial Z}(Z = 0) = \sqrt{\frac{(1 + b\xi)}{\pi\theta}}, \quad (20)$$

where the magnitude of the dimensionless flux is defined as

$$\frac{\partial \Phi}{\partial Z}(Z = 0) = \frac{N_A}{\varepsilon_y D_{\text{eff}} C_{g0}/L} \quad (21)$$

and the magnitude of the flux of VOC at the soil surface is

$$N_A = \varepsilon_y D_{\text{eff}} \frac{\partial C_g}{\partial z}(z = 0). \quad (22)$$

The use of this short-time analytical solution (Eq. (20)), as opposed to an analytical solution which is valid for all times in a finite-depth soil column, is appropriate here for validating the accuracy of the numerical solution, because the numerical solution was used exclusively at relatively short times.

### 2.3. Linearization of diffusion equation (7)

In the field, there may be great value in estimating the flux of VOC to the atmosphere from air-dry surface soils exhibiting nonlinear sorption using an approximate analytical solution. To develop the approximate analytical solution, a linearization of the governing equation for diffusion and nonlinear sorption will be used. Linearization of the diffusion equation has been reported in the literature for the diffusion of carbon tetrachloride (CTET) through soil-bentonite cut-off barriers [11] by approximating the sorption of CTET as linear over a specified concentration range rather than as a Freundlich sorption isotherm. The errors in making this approximation were not reported in that paper and it is the intention here to evaluate the errors in making this assumption for a linearization method of BET sorption and diffusion in air-dry soil.

In the linearization step, the derivative of the dimensionless BET sorption isotherm in Eq. (7) is replaced with the slope of a linear isotherm, where the slope is defined by

$$K'' = \xi \frac{U_A/U_{Am}}{\Phi} \quad \text{at } \Phi = 1 = \xi \frac{b\delta[1 - (n+1)\delta^n + n\delta^{(n+1)}]}{(1-\delta)[1 + (b-1)\delta - b\delta^{(n+1)}]}, \quad (23)$$

evaluated at  $\Phi = 1$ .

With this definition of  $K''$  substituted into Eq. (7), the dimensionless continuity equation becomes

$$(1 + K'') \frac{\partial \Phi}{\partial \theta} = \frac{\partial^2 \Phi}{\partial Z^2}. \quad (24)$$

The analytical solution for the dimensionless emission rates can be easily obtained, when the solution is restricted to short times, as [20]

$$\frac{\partial \Phi}{\partial Z}(Z = 0) = \frac{\sqrt{(1 + K'')}}{\sqrt{\pi \theta}} \quad (25)$$

In order to determine the accuracy of this solution to the linearized equation, the dimensionless emission rates were evaluated at the soil surface ( $\partial \Phi / \partial Z (Z = 0)$ ) using Eq. (25) and were then compared to those obtained from the numerical solution to Eq. (7).

### 3. Results and discussion

Numerical solutions of Eqs. (7)–(11) were computed for diffusion and nonlinear sorption of benzene in Auberry sandy loam and Kettleman Hills soil using the BET sorption parameters and the physical and chemical properties for the soils and benzene [13]. Table 1 contains these parameters. The physical properties of the two soils are comparable except for the BET sorption parameters, where Kettleman Hills soil has a much higher sorption capacity, much stronger sorption energy, but fewer sorbed layers of benzene. In the dilute limit, the numerical solution to Eq. (7) (linear sorption case) was in excellent agreement with the dimensionless VOC predictions using Eq. (20). Because the numerical solution was accurate in the dilute limit case, it was also assumed to be accurate for the more general case of nonlinear sorption.

#### 3.1. Effects of $\delta$

By varying the value of the dimensionless initial gas-phase concentration of VOC in soil,  $\delta$ , a family of dimensionless BET sorption functions was generated and used as input to the numerical solution of Eq. (7). Fig. 2 shows several of these isotherms, which were generated utilizing the sorption isotherm parameters for benzene and

Table 1

BET sorption parameters and soil physical properties for Auberry sandy loam and Kettleman Hills soil with benzene as the VOC<sup>a</sup>

	Auberry	Kettleman
$C_{AS}$ (mg benzene/cm <sup>3</sup> vapor) <sup>b</sup>	0.396	0.396
$\rho_B$ (g soil/cm <sup>3</sup> soil)	1.28	1.21
$\varepsilon_v$ (cm <sup>3</sup> vapor/cm <sup>3</sup> soil)	0.50	0.54
$U_{Am}$ (mg benzene/g soil)	0.896	5.798
$b$	8.883	17.798
$n$	15	5.6

<sup>a</sup> Shonnard et al. [13].

<sup>b</sup> Calculated from the correlation in Reid et al. [21].

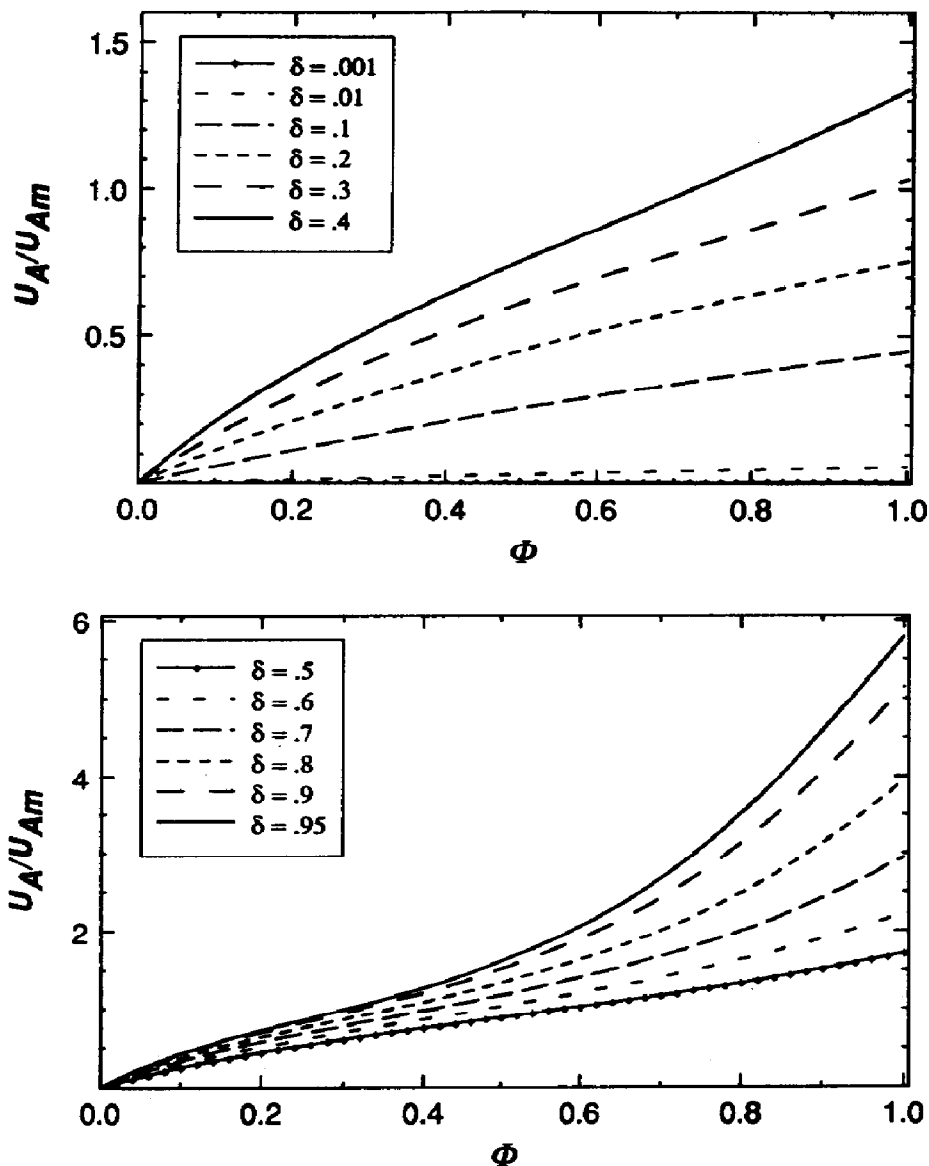


Fig. 2. Dimensionless BET sorption isotherms for benzene and Auberry sandy loam for several values of  $\delta$ . Sorption parameters are taken from Table 1. These dimensionless isotherms were used as input to the numerical solution of Eq. (7).

Auberry sandy loam in Table 1. Input parameters to the numerical solution, calculated from these sorption isotherms and the data in Table 1, include the dimensionless sorption parameter given by Eq. (12),  $\xi$ ; the dimensionless initial gas-phase concentration of VOC in soil,  $\delta$ ; and the maximum number of sorbed molecular layers,  $n$ .

The results of the simulations for the diffusion and nonlinear sorption of benzene in Auberry sandy loam are shown in Figs. 3-5. Fig. 3 shows the dimensionless gas-phase concentration profiles obtained from the numerical solution of Eq. (7) at



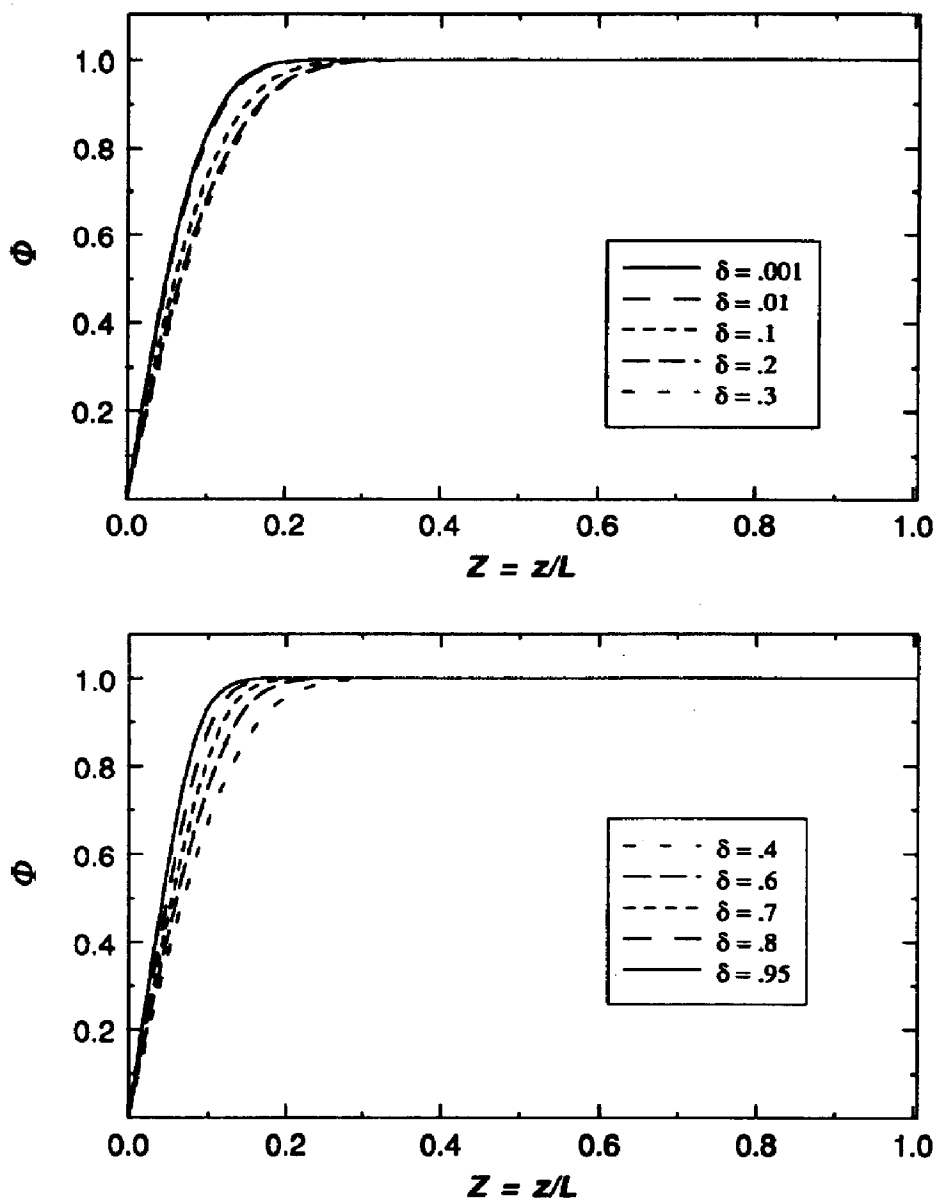


Fig. 3. Dimensionless soil gas-phase concentration profiles ( $\Phi$ ) for benzene diffusion and BET sorption in Auberry sandy loam at several values of  $\delta$ . All  $\Phi$  profiles were taken at dimensionless time,  $\theta = 0.1$ . Dimensionless isotherms from Fig. 2 were used in the numerical solution.

a dimensionless time of  $\theta = 0.1$ . The effect of increasing the initial gas-phase concentration,  $\delta$ , from 0.001 to 0.3 was to cause a deeper penetration of  $\Phi$  into the soil column. Conversely, as  $\delta$  was increased from 0.3 to 0.95,  $\Phi$  penetrated into the soil column to a progressively smaller extent. The total-soil concentration,  $C_T$ , is the sum of the gas-phase concentration and the sorbed-phase concentration in a unit volume of soil. The dimensionless total-soil concentration profiles,  $\Phi_T$ , for benzene diffusion in Auberry sandy loam are shown in Fig. 4 at a dimensionless time of  $\theta = 0.1$ . With an increase in  $\delta$  from 0.001 to 0.4, there was an increase in the penetration of  $\Phi_T$  into the

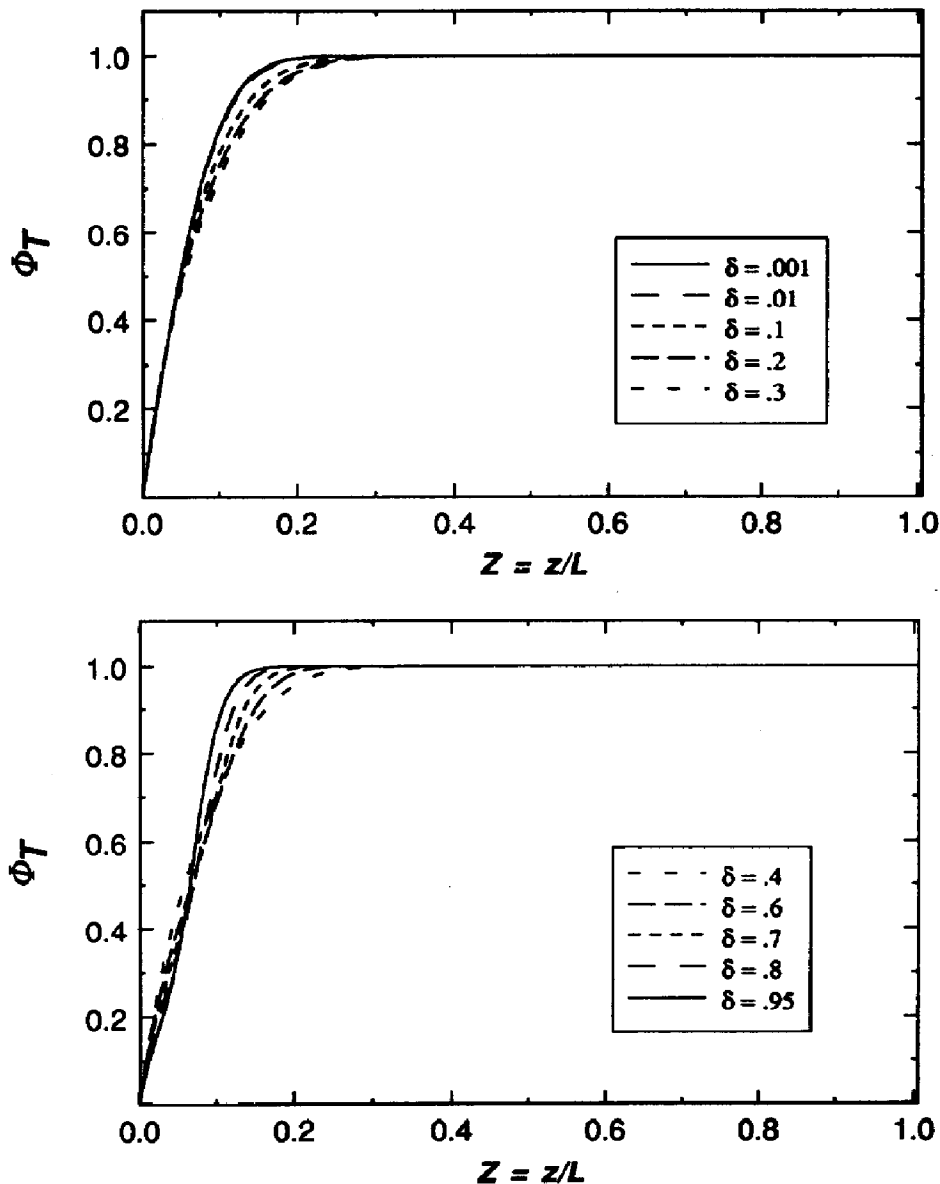


Fig. 4. Dimensionless total-soil concentration profiles ( $\Phi_T$ ) for benzene diffusion and BET sorption in Auberry sandy loam at several values of  $\delta$ . All  $\Phi_T$  profiles were taken at dimensionless time,  $\theta = 0.1$ . Dimensionless isotherms from Fig. 2 were used in the numerical solution.

soil and from  $0.4 < \delta < 0.95$  the opposite trend occurred. The reason for these trends in the dimensionless concentration profiles is due to the curvature of the BET sorption isotherm of VOC in air-dry soils, which are concave downward to the horizontal axis (relative concentration) at small values of  $\delta$  ( $0 \leq \delta \leq 0.3$ ) and concave upward at higher values ( $0.3 \leq \delta \leq 1$ ). Thus, as  $\delta$  increases from 0 to 0.3, the proportion of sorbed VOC decreases relative to the amount of VOC initially in the vapor, and this relative deficiency of sorbed VOC results in a diminished retardation of VOC diffusive

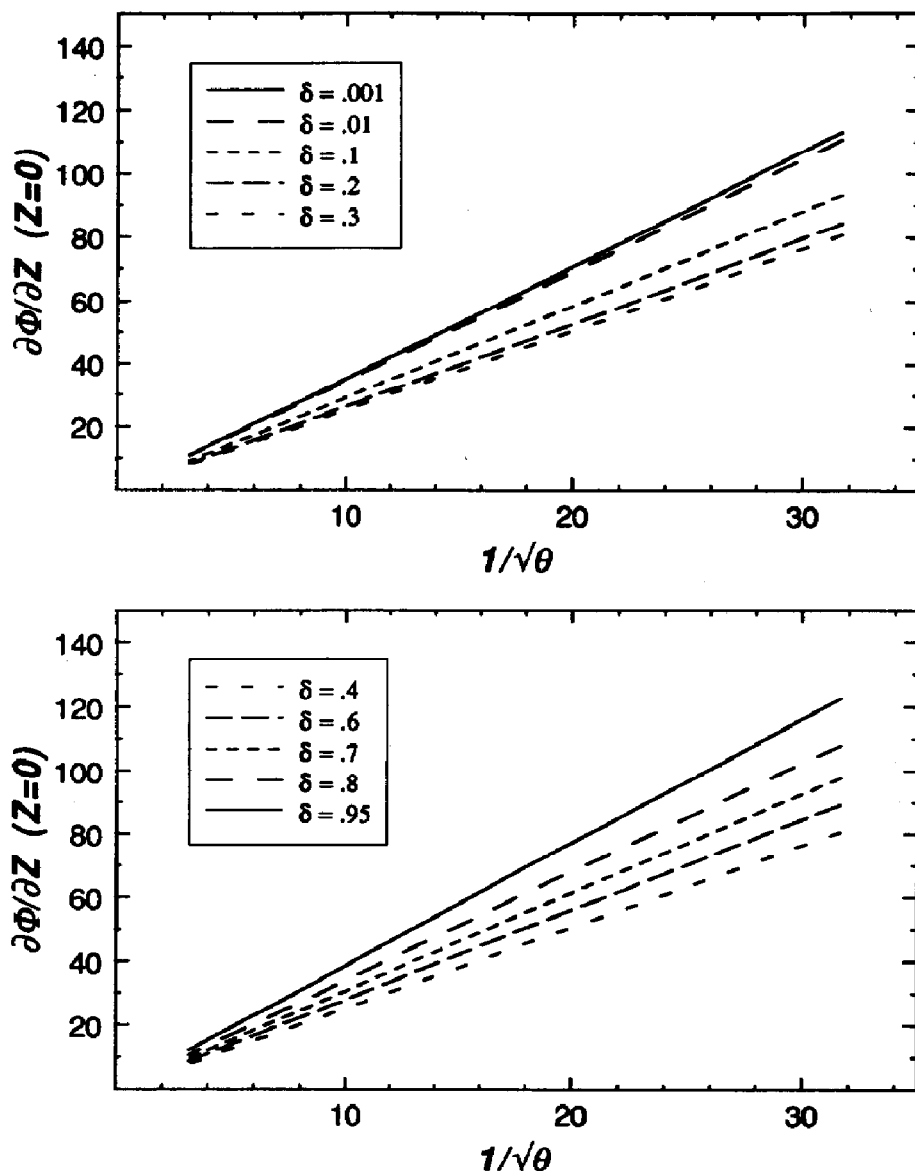


Fig. 5. Dimensionless soil surface emission rates of benzene from Auberry sandy loam at several values of  $\delta$ . Dimensionless isotherms from Fig. 2 were used in the numerical solution.

transport and a deeper penetration of the concentration profiles into the soil after a specified time period. The opposite occurs at higher values of  $\delta$  ( $0.3 \leq \delta \leq 1$ ).

The dimensionless emission rates versus  $1/\sqrt{\theta}$  are shown in Fig. 5. The dimensionless emission rates were linear when plotted in this fashion, as expected from analyses presented in many texts [20]. This is verification that the emission rates resulting from diffusion and nonlinear sorption of VOC from soil are inversely proportional to  $\sqrt{\theta}$ , regardless of the degree of nonlinear sorption. The dimensionless emission rates decreased with increasing  $\delta$  when the dimensionless uptake curves shown in

Fig. 2 were concave downward ( $0.001 \leq \delta \leq 0.3$ ). They increased with increasing  $\delta$  when the dimensionless uptake curves were concave upward ( $0.3 \leq \delta \leq 0.95$ ).

A short example will emphasize the importance of accounting for nonlinear sorption when calculating VOC emissions from contaminated air-dry soils. Utilizing the results shown in Fig. 5, emission rates of benzene,  $N_A$  ( $A = \text{benzene}$ ), from a uniformly contaminated Auberry sandy loam will be determined using Eq. (21). The total depth of uniform soil contamination is assumed to be  $L = 100$  cm, the void fraction in the soil is  $\varepsilon_v = 0.50$ , and the effective diffusivity is  $D_{\text{eff}} = D_{\text{AB}} \varepsilon_v^{1/3} = (0.088 \text{ cm}^2/\text{s})(0.50)^{1/3} = 0.070 \text{ cm}^2/\text{s}$ . In the first case, linear sorption is considered and a value of  $\delta = 0.001$  is used (linear sorption in the dilute limit of BET sorption), and therefore,  $C_{g0} = \delta C_{\text{AS}} = (0.001)(0.396 \text{ mg benzene}/\text{cm}^3 \text{ gas}) = 3.96 \times 10^{-4} \text{ mg benzene}/\text{cm}^3 \text{ gas}$ . Fig. 5 shows that at  $1/\sqrt{\theta} = 10$ , the dimensionless benzene flux is 35.2 for  $\delta = 0.001$ . For this value of  $\theta$ , the elapsed time is 23.8 min as obtained from Eq. (6). From Eq. (21), the benzene emission flux from the soil is  $N_A = 4.88 \times 10^{-6} \text{ mg benzene}/(\text{cm}^2 \text{ s}) = 0.176 \text{ g benzene}/(\text{m}^2 \text{ h})$ . The case of nonlinear sorption of benzene is considered next. A value of  $\delta = 0.1$  is chosen, and therefore  $C_{g0} = \delta C_{\text{AS}} = (0.1)(0.396 \text{ mg benzene}/\text{cm}^3 \text{ gas}) = 3.96 \times 10^{-2} \text{ mg benzene}/\text{cm}^3 \text{ gas}$ . Fig. 5 shows that at  $1/\sqrt{\theta} = 10$ , the dimensionless benzene flux is 29.2. From Eq. (21), the benzene emission flux from the soil is  $N_A = 4.05 \times 10^{-4} \text{ mg benzene}/(\text{cm}^2 \text{ s}) = 14.57 \text{ g benzene}/(\text{m}^2 \text{ h})$ . Although the initial soil-vapor concentration in these two cases increased by a factor of 100 ( $\delta = 0.001$  to  $\delta = 0.1$ ), the emission flux increased by a factor of only  $14.57/0.176 = 82.8$ . This relatively diminished emission flux for  $\delta = 0.1$  occurs because the amount of sorbed benzene increases by less than a factor of 100 as  $\delta$  increases by a factor of 100 for BET sorption in this concave downward portion of the sorption isotherm. Had linear sorption been assumed in these model simulations, all lines in Fig. 5 would be coincident with the  $\delta = 0.001$  line and we would have calculated a higher value of the benzene flux for the  $\delta = 0.1$  case ( $N_A = 17.6 \text{ g benzene}/(\text{m}^2 \text{ h})$ ). Thus, an error of  $(17.6-14.57)/14.57 (100) = 20.8\%$  results if nonlinear sorption is ignored.

### 3.2. Effects of BET parameters

Simulations were conducted in order to determine the sensitivity of the model to differences in the BET sorption parameters ( $U_{\text{Am}}, b, n$ ) for Auberry sandy loam and Kettleman Hills soil. The main results of these simulations are summarized without graphical presentation. Because benzene sorbs to Kettleman Hills soils to a much greater degree than to Auberry sandy loam, as indicated by a much larger value of  $U_{\text{Am}}$  for Kettleman soil (see Table 1), a longer dimensionless time was required in the simulations ( $\theta = 1$  for Kettleman versus  $\theta = 0.1$  for Auberry) for comparable penetration of  $\Phi$  or  $\Phi_T$  into the soil. This reflects the ability of Kettleman Hills soil to retard the diffusive transport of VOC due to the increased sorptive capacity of its mineral surfaces.

The numerical simulations demonstrated that, over the range  $0 \leq \delta \leq 0.3$ , there was an effect of the BET sorption energy parameter,  $b$ , on the soil profiles of  $\Phi$  and

$\Phi_T$  and on the dimensionless emission rates. In addition, the effects increased for the larger  $b$ . In comparing the two different soils, the value of the BET sorption energy parameter,  $b$ , for Kettleman is approximately two times the value for Auberry. The effect of  $b$  in Kettleman Hills soil was to cause more than a doubling of the penetration of  $\Phi$  and  $\Phi_T$  into the soil as  $\delta$  increased from 0.001 to 0.3, from a dimensionless soil depth of  $Z = 0.15-0.41$ . In comparison, for Auberry sandy loam (Figs. 3 and 4) the increase in penetration was from  $Z = 0.19$  to 0.28. In addition, for Kettleman Hills soil the simulations predicted a decrease in the dimensionless emission rates by 60.5% as  $\delta$  increased from 0.001 to 0.3, whereas for Auberry sandy loam the decrease was only 28.9%.

The numerical results showed that, over the range  $0.3 \leq \delta \leq 0.95$ , there was an effect of  $n$ , the maximum number of sorbed molecules, on the profiles of  $\Phi$  and  $\Phi_T$  and on the dimensionless emission rates. As shown in Figs. 3 and 4 for Auberry sandy loam ( $n = 15$ ), as  $\delta$  increased from 0.3 to 0.95, there was a decrease in the penetration of the profiles of  $\Phi$  and  $\Phi_T$  into the soil from  $Z = 0.28$  to 0.13. For Kettleman Hills soil ( $n = 5.6$ ), this decrease was smaller ( $Z = 0.40-0.35$ ). For Auberry sandy loam, as shown in Fig. 5, there was an increase in the dimensionless emission rates of 40.7% over this range of  $\delta$ . For Kettleman Hills soil ( $n = 5.6$ ), the increase in the dimensionless emission rates was only 6.6%.

The effect of a large value of  $n$  on  $\Phi_T$  is shown in Fig. 6 for diffusion of benzene in Kettleman Hills soil. The upper graph shows the dimensionless BET sorption isotherms used in the simulations for  $n = 100$  over the range  $0.5 \leq \delta \leq 0.95$ . The lower graph is a plot of  $\Phi_T$  versus  $Z$ , and as  $\delta$  increased from 0.5 to 0.95 the penetration of  $\Phi_T$  into the soil decreased, as expected; however the shape of the concentration profiles approached a step function. At the highest values of  $\delta$ , the penetration of  $\Phi_T$  into the soil proceeded as though there were evaporation of benzene from a receding liquid front. This interpretation of the diffusion process is intuitively appealing because at such high numbers of sorbed layers (e.g.  $n = 100$ ), the sorbed phase begins to resemble a bulk liquid phase.

### 3.3. Evaluation of the linearized model

A linearized model of VOC diffusion from air-dry soil was evaluated for the accuracy in predicting the dimensionless emission rates. The linearization step allows the substitution of a linear sorption isotherm for the nonlinear BET sorption isotherm in Eq. (7), as shown graphically in Fig. 7, for the case of benzene sorption to Auberry sandy loam. Comparisons of the dimensionless emission rates for the numerical solution of Eq. (7) with the analytical solution of the linearized model, Eq. (25), were made and a correction factor was defined as the ratio of these dimensionless emission rates:

$$\frac{\partial \Phi / \partial Z (Z = 0) \text{ BET model equation (7)}}{\partial \Phi / \partial Z (Z = 0) \text{ linearized model equation (25)}} = \text{correction factor.} \quad (26)$$

Fig. 8 shows the correction factors for the linearized diffusion and sorption model at several values of  $\delta$ . The deviations of the linearized model of diffusion and

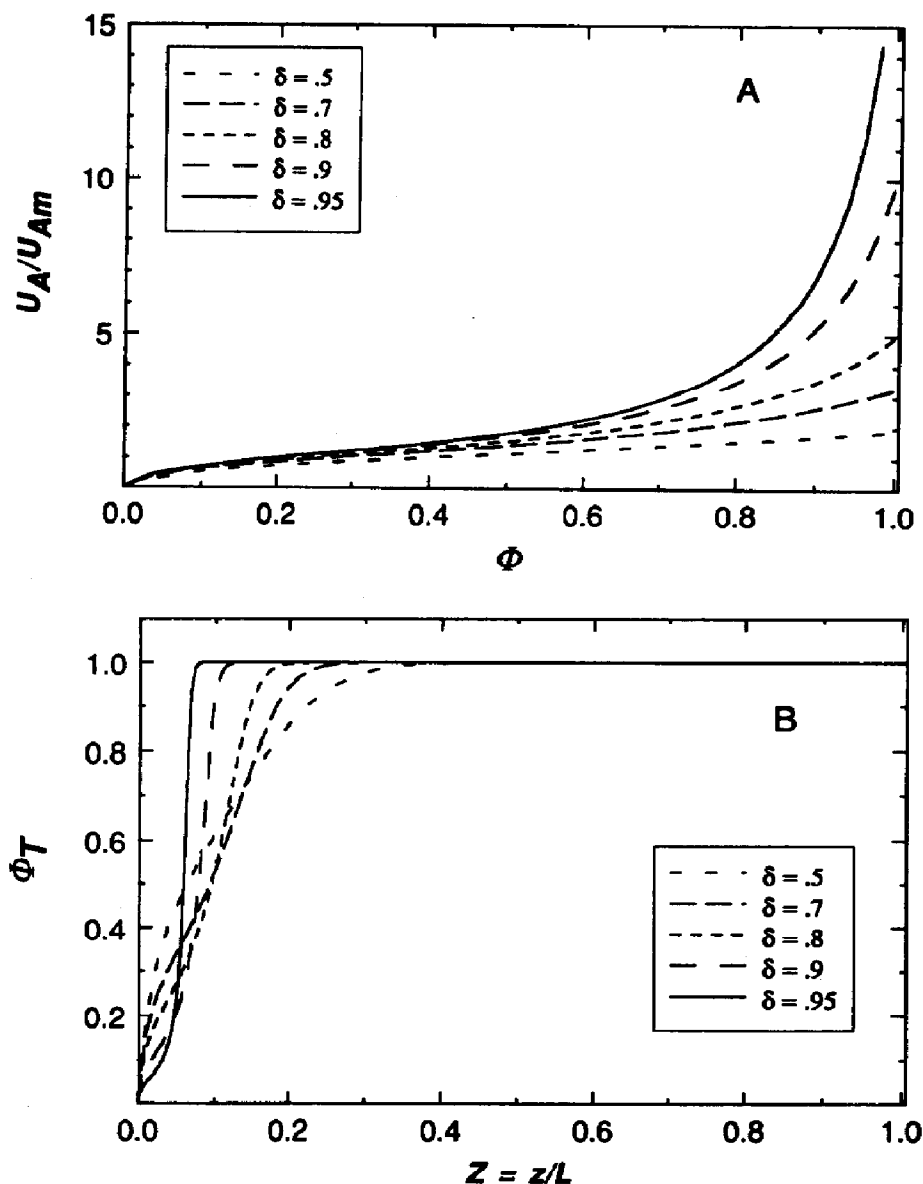


Fig. 6. The effects of a large number of sorbed benzene layers ( $n = 100$ ) on the dimensionless total-soil concentration profile in Kettleman Hills soil at several values of  $\delta$ . Graph A represents the dimensionless isotherms used in the numerical solution. Graph B represents the dimensionless total-soil concentration profiles.

sorption of benzene for both Kettleman Hills soil and Auberry sandy loam did not exceed 20% deviation in the dimensionless emission rates for any of the cases studied. This margin of error may be acceptable for many environmental problems concerning VOC emission from air-dry contaminated soils, because the uncertainties in soil properties may easily exceed 20% in the field, thereby diminishing the significance of the linearization error. Further evaluation of the linearized model demonstrated

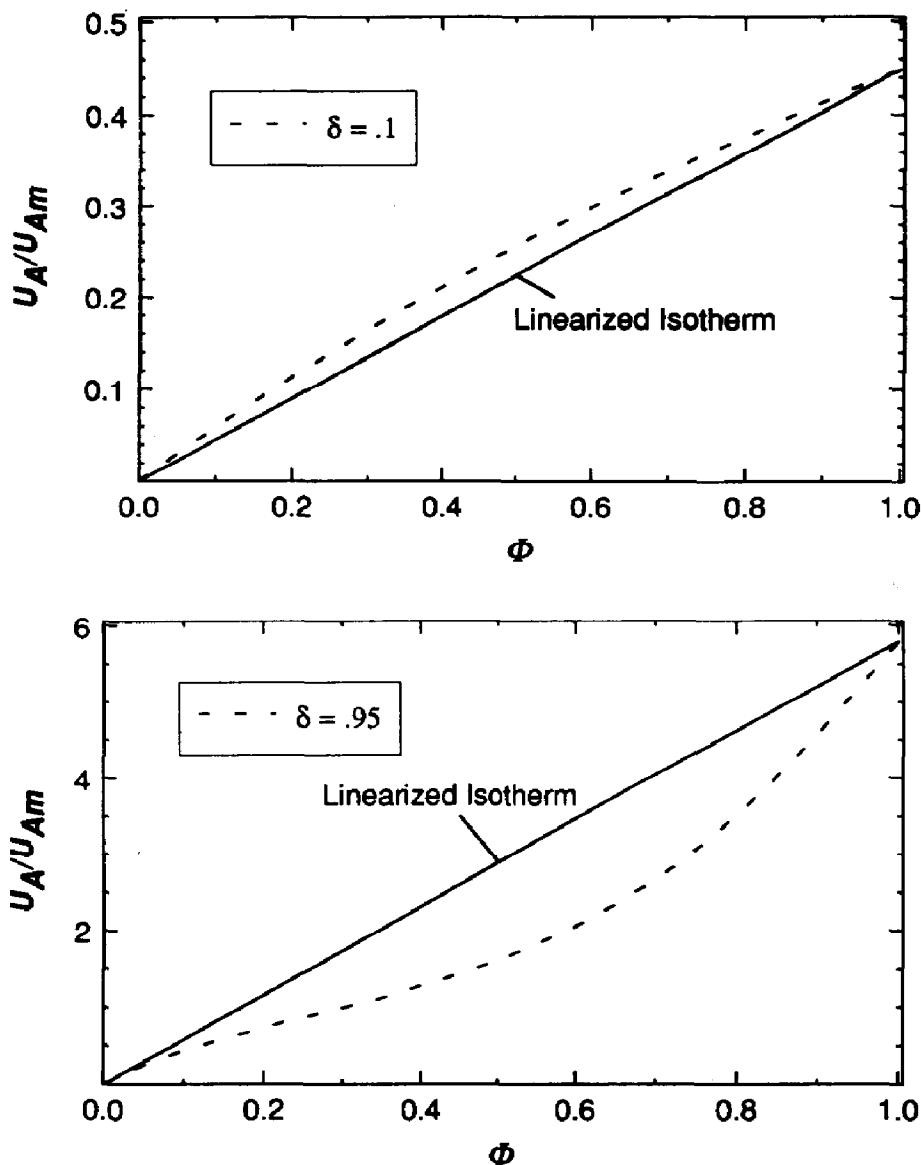


Fig. 7. Dimensionless linear sorption isotherms (—) used in the linearized diffusion model (Eq. (25)). Dimensionless BET isotherm (-----) used in the numerical solution to Eq. (7).

comparable accuracy in the dimensionless gas-phase and total-soil concentration profiles. The solution to the linearized model is much simpler than the exact numerical solution and requires much less time to compute. The same strategy for evaluating the accuracy of the solutions to linearized diffusion models can be applied to situations where other types of nonlinear sorption isotherms are encountered, such as Freundlich and Langmuir sorption isotherms for soils where higher water-saturation conditions are encountered.

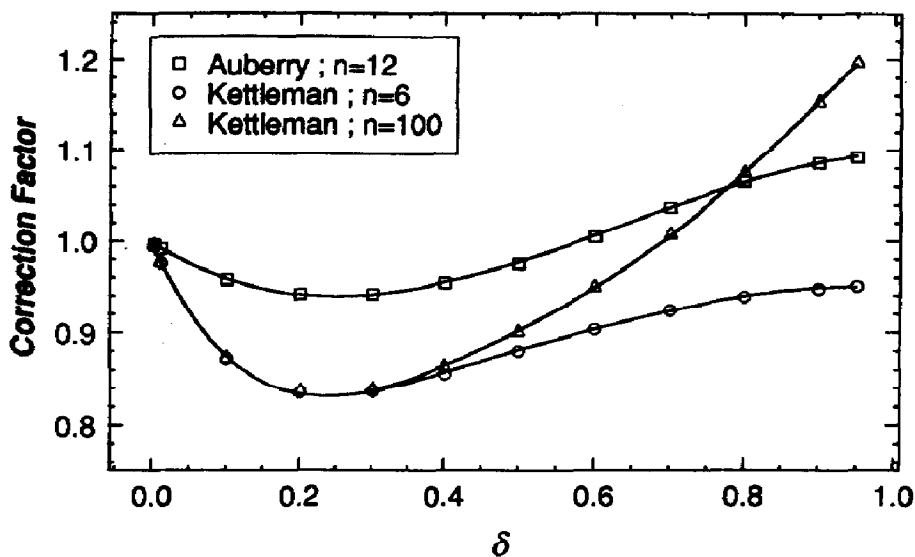


Fig. 8. Correction factors to the linearized diffusion model for benzene diffusion in Auberry sandy loam and Kettleman Hills soil as a function of  $\delta$ .

#### 4. Summary and conclusions

Because in many field situations, VOCs which volatilize from soils to the atmosphere must transverse an air-dry soil layer, diffusion and sorption in air-dry soils is a topic of interest in environmental science and engineering. In this article, benzene diffusion in two air-dry soils having significantly different mineral surface areas was studied theoretically. The numerical simulations demonstrated that a variation in the retardation of VOC diffusive transport occurred with changes in initial gas-phase concentration,  $\delta$ , and with BET sorption parameters,  $b$  and  $n$ . This is in clear contrast with the case of *linear* sorption where there is no change in diffusive retardation with soil VOC concentration level. The effects of  $b$  and  $n$  were over the ranges  $0 \leq \delta \leq 0.3$  and  $0.3 \leq \delta \leq 1$ , respectively, in terms of changes to the dimensionless gas-phase and total-soil concentration profiles and to the dimensionless emission rates to the atmosphere. One example calculation for benzene emission from a coarse-textured sandy loam showed that a 20% error in estimating emissions occurred when linear sorption was assumed in a situation where nonlinear sorption clearly occurred. Errors will certainly vary depending upon the particular VOC and soil. Also, a linearization of the governing equation of diffusion and nonlinear BET sorption was performed and the resulting analytical solution accounted for the effects of nonlinear BET sorption to within 20% of the correct numerical solution for all cases studied.

The air-dry soil layer at the soil-atmosphere interface is very important because of its effects on VOC volatilization from contaminated soils to the atmosphere and on dry deposition of airborne VOC to clean soils. This is especially true in arid climates,



where soil mineral surfaces dominate sorption and where competitive sorption between water and VOC can be strongly influenced by short-term variations in soil temperature and relative humidity. Further research is needed to evaluate the importance of the air-dry soil layer in controlling and modifying the rate of emission of VOCs to the atmosphere from contaminated soils.

## Notation

$b$	BET energy parameter
$C_{AS}$	saturation concentration of VOC at temperature $T$ (g VOC/cm <sup>3</sup> gas)
$C_g$	volume-averaged gas-phase soil concentration (g VOC/cm <sup>3</sup> gas)
$C_{g0}$	volume-averaged initial gas-phase soil concentration (g VOC/cm <sup>3</sup> gas)
$C_T$	volume-averaged total-soil concentration (g VOC/cm <sup>3</sup> soil)
$D_{AB}$	molecular diffusivity of the VOC (A) in air (B) (cm <sup>2</sup> /s)
$D_{app}$	apparent diffusivity of VOC in soil (cm <sup>2</sup> /s)
$D_{eff}$	effective diffusivity of VOC in the soil-vapor space (cm <sup>2</sup> /s)
$\Delta H_a$	enthalpy of sorption for the first sorbed layer (kcal/mol VOC)
$\Delta H_v$	enthalpy of vaporization of liquid VOC (kcal/mol VOC)
$K''$	dimensionless linear sorption coefficient in the linearized diffusion model
$L$	depth of soil column (cm)
$n$	maximum number of sorbed molecular layers
$R$	ideal gas constant (kcal/(mol K))
$t$	time (s)
$T$	temperature (K)
$U_A$	the BET uptake of VOC by the soil (g VOC/g soil solids)
$U_{Am}$	monolayer uptake of VOC to soil (g VOC/g soil solids)
$z$	soil depth coordinate (cm)
$Z$	dimensionless soil depth
$\delta$	dimensionless initial gas-phase concentration of VOC
$\epsilon_v$	soil void fraction
$\Phi$	dimensionless gas-phase soil concentration of VOC
$\Phi_T$	dimensionless total-soil concentration of VOC
$\theta$	dimensionless time
$\rho_B$	soil bulk density (g soil solids/cm soil)
$\xi$	the dimensionless BET sorption parameter

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