An analytical model for *in situ* extraction of organic vapors

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Abstract

This paper introduces a simple convective-flow model that can be used as a screening tool and for conducting sensitivity analyses for *in situ* vapor extraction of organic compounds from porous media. An assumption basic to this model was that the total mass of volatile organic chemicals (VOC) exists in three forms: as vapors, in the soil solution, and adsorbed to soil particles. The equilibrium partitioning between the vapor–liquid phase was described by Henry's law constants (K_H) and between the liquid-soil phase by soil adsorption constants (K_d) derived from soil organic carbon–water partition coefficients (K_{oc}). The model was used to assess the extractability of 36 VOCs from a hypothetical site. Most of the VOCs appeared to be removable from soil by this technology, although modeling results suggested that rates for the alcohols and ketones may be very slow. In general, rates for weakly adsorbed compounds ($K_{oc} < 100$ mL/g) were significantly higher when K_H was greater than 10^{-4} atm-m^3-mol^{-1}. When K_{oc} was greater than about 100 mL/ g, the rates of extraction were sensitive to the amount of organic carbon present in the soil. The air permeability of the soil material (k) was a critical factor. *In situ* extraction needs careful evaluation when k is less than 10 millidarcies to determine its applicability. An increase in the vacuum applied to an extraction well accelerated removal rates but the diameter of the well had little effect. However, an increase in the length of the well screen open to the contaminated zone significantly affected removal rates, especially in low-permeability materials.

Introduction

Soils and other surficial materials can become contaminated with volatile organic chemicals (VOCs) from the land disposal of hazardous wastes, chemical spills, or leaking storage tanks. The migration of vapors from these sources can result in relatively large volumes of contaminated, subsurface materials, and some type of site remediation may be required. *In situ* vapor extraction or volatilization is a relatively new technology whereby air is injected and/or withdrawn from the subsurface through some type of system that conducts the vapors to the surface for treatment or discharge. Volatile organic chemicals are then gradually removed as air sweeps through the contaminated zone.

In situ extraction has been successfully applied in site restorations, but the-

oretically based design equations that define the limits and behavior of this technology are lacking [1,2]. Consequently, the design and application of *in situ* extraction has been empirical [2,3]. The purpose of this study was to assess the feasibility of *in situ* extraction of VOCs from the vadose zone by applying a simple convective-flow model to various contaminant extraction scenarios.

Approach

Derivation of the exponential-removal model

It was assumed that the total mass of contaminant per volume of soil (M) exists in three phases:

$$M = M_v + M_d + M_a \tag{1}$$

where M_v is the mass of VOC in the vapor phase, M_d is the mass of VOC in the interstitial liquid, and M_a is the mass of VOC adsorbed to solid phases.

It was assumed that the equilibrium distribution of the vapor phase concentration (C_v) and the concentration in the liquid phase (C_d) are described by a dimensionless vapor–liquid partition coefficient; $C_v/C_d = K_v$. It was further assumed that the adsorption–desorption behavior of VOCs could be described by a linear and reversible adsorption isotherm where K_d is the adsorption constant and C_a is the amount of VOC adsorbed per mass of adsorbent, viz. $C_a/C_d = K_d$. If eq. (1) is cast on a mass VOC per volume basis, it becomes

$$C_t = \eta_a C_v + \eta_l C_d + K_d \rho_b C_d \tag{2}$$

where η_a is the air-filled porosity, η_l is the liquid-filled porosity, and ρ_b is the dry bulk density of the soil material.

If eq. (2) is recast in terms of C_v, it may be given as

$$C_v/C_t = [(K_d\rho_b/K_v) + (\eta_l/K_v) + (\eta_t - \eta_l)]^{-1} \tag{3}$$

where C_t is total VOC concentration, and η_t is total porosity.

Equation (3) has been defined as the strippability relationship [4].
It describes the simultaneous partitioning of a VOC between vapor, liquid, and solid phases in the unsaturated zone.

As air moves through the contaminated zone, the organic vapors are displaced and it is assumed that the change in mass in the vapors equals the total change in mass, viz.,

$$\Delta m = -C_v \Delta V \tag{4}$$

where m is the mass of vapors, and V is the volume of air moved through the soil.

Hence, the equilibrium relationships between the three phases (vapor, liquid, and adsorbed) are disrupted by the air sweeping. It was assumed that the

system will reequilibrate by the volatilization of VOCs from the liquid phase and by desorption from the solid phases. The reaction rates were assumed to be instantaneous, and thus kinetic limitations such as the diffusion rates of VOCs in liquids were explicitly ignored. Experimental measurements have suggested that the rate of volatilization of trichloroethene in unsaturated soil columns is rapid, and that equilibrium can be assumed [5]. This assumption must, however, be used with caution. Smith et al. [6] proposed that a lack of trichloroethene-vapor equilibrium in a field study was the result of the slow desorption rate from organic matter in the vadose zone.

The differential form of eq. (4) is

$$dm = -C_v dV \tag{5}$$

If the right-hand side of eq. (3) is designated as α, then

$$dm/m = [-\alpha(\eta_t - \eta_l)/V_a]dV, \tag{6}$$

since total volume of soil may be written as $V_a/(\eta_t - \eta_l)$ where V_a is the total volume of air in the pore spaces.

If the left side of eq. (6) is integrated from the initial mass of VOC present (m_0) to the amount remaining at time t (m_t), and the right-hand side from the initial volume of air passed through the contaminated zone (assumed to be zero) to the accumulative volume of air (V_t) at time t, eq. (6) yields

$$\int_{m_0}^{m_t} dm/m = \frac{-\alpha(\eta_t - \eta_l)}{V_a} \int_0^{V_t} dV \tag{7}$$

hence

$$\ln(m_t/m_0) = -\alpha(\eta_t - \eta_l)(V_t/V_a) \tag{8}$$

or

$$m_t/m_0 = \exp[-\alpha(\eta_t - \eta_l)(V_t/V_a)] \tag{9}$$

Equation (9), designated as the exponential removal model, was used in this study to evaluate the removal of volatile organic compounds *in situ* extraction. The general form of this model is analogous to a soil column acting as a completely mixed reactor [7,8]. This specific model was presented by Hydro Geo Chem [9] and applied in an evaluation of *in situ* extraction at a hazardous waste site. Hochmuth et al. [10] also derived an exponential removal-type model for *in situ* extraction, which was coupled with a companion equation that described diffusion.

Hypothetical site model

To test the exponential removal model, a hypothetical site was defined (Fig. 1) that consisted of a single, vertical extraction well placed in a volume of ho-

mogeneous, isotropic, isothermal, and unsaturated soil material. The partial vacuum applied to the well induces air flow from the effective radius (r_e) towards the open interval of the well. The isothermal, steady-state flow of air through the material as a result of a pressure gradient was estimated by the expression of Al-Hussainy et al. [11] and Al-Hussainy and Ramey [12], viz.,

$$Q = [8.64\pi k(P_e^2 - P_w^2)]/[P_a\mu\ln(r_e/r_w)] \tag{10}$$

where Q is the flow rate of air (m^3/m-d), k is air permeability (darcies), P_e is the air pressure at the effective radius (i.e., 1 bar), P_w is the air pressure in the well (i.e., the partial vacuum, bar), P_a is the ambient air pressure (i.e., 1 bar), μ is air viscosity (cP or mPa-s), r_w is the radius of extraction well (m), r_e is the effective radius (radius of influence of the partial vacuum in m), and the factor 8.64 converts cm^3/cm-s to m^3/m-d.

Equation (10) was also used by Hydro Geo Chem [9], and was derived for engineering-scale approximation, and does not take into account pressure-dependent gas properties.
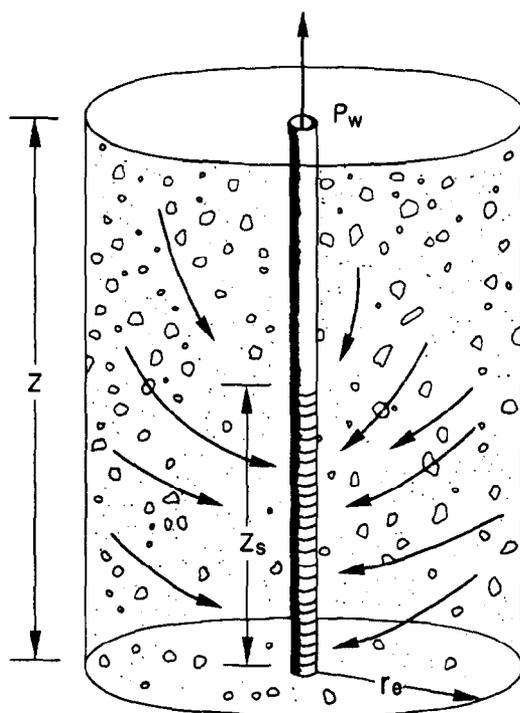

Fig. 1. The hypothetical site consisting of a cylindrical volume of unsaturated, homogeneous, isothermal porous material with a single extraction well of length Z, and a screened or open interval, of Z_s. The decreased atmospheric pressure in the well (P_w) induces air flow from the effective radius (r_e) to the well.

TABLE 1

Appendix I volatile organic compounds [21], soil organic carbon–water partition coefficients (K_{oc}) and Henry's law coefficient (K_H)

Compound	K_{oc} (source) (mL/g)		K_H (source) (atm-m^3-mol^{-1})	
Acetone	1	(1)	6.8×10^{-6}	(2)
Acrolein	4	(3)	7.8×10^{-5}	(4)
Acrylonitrile	9	(3)	8.8×10^{-5}	(4)
Benzene	83	(5)	5.6×10^{-3}	(2)
Bromochloromethane	ND		ND	
Bromodichloromethane	ND		1.6×10^{-3}	(6)
4-Bromofluorobenzene	ND		ND	
Bromoform	60	(3)	4.3×10^{-4}	(6)
Bromomethane	23	(3)	6.4×10^{-3}	(7)
2-Butanone (methyl ethyl ketone)	4	(1)	2.4×10^{-5}	(2)
Carbon disulfide	63	(1)	1.2×10^{-4}	(2)
Carbon tetrachloride	232	(1)	3.0×10^{-2}	(8)
Chlorobenzene	318	(1)	3.9×10^{-3}	(2)
Chlorodibromomethane	ND		8.7×10^{-4}	(6)
Chloroethane	42	(3)	1.1×10^{-2}	(8)
2-Chloroethyl vinyl ether	ND		ND	
Chloroform	34	(3)	3.7×10^{-3}	(8)
Chloromethane	25	(1)	8.8×10^{-3}	(8)
Dibromomethane	27	(3)	8.9×10^{-4}	(7)
1,4-Dichloro-2-butane	ND		ND	
Dichlorodifluoromethane (F-12)	269	(1)	4.3×10^{-1}	(2)
1,1-Dichloroethane	43	(3)	5.6×10^{-3}	(8)
1,2-Dichloroethane	36	(3)	1.3×10^{-3}	(7)
1,1-Dichloroethene	58	(3,9)	2.6×10^{-2}	(8)
trans-1,2-Dichloroethene	169	(3)	9.4×10^{-3}	(8)
cis-1,3-Dichloropropene	23	(3)	2.3×10^{-3}	(4)
trans-1,3-Dichloropropene	26	(3)	1.8×10^{-3}	(4)
1,4-Difluorobenzene	ND		ND	
Ethanol	1	(3)	6.3×10^{-6}	(7)
Ethylbenzene	622	(1)	8.7×10^{-3}	(7)
Ethyl methacrylate	ND		ND	
2-Hexanone	14	(3)	7.5×10^{-6}	(4)
Iodomethane	ND		5.5×10^{-3}	(7)
Methylene chloride	25	(1)	3.2×10^{-3}	(2)
4-Methyl-2-pentanone	24	(1)	1.3×10^{-4}	(2)
Styrene	260	(3)	2.3×10^{-4}	(4)
1,1,2,2-Tetrachloroethane	88	(3)	4.6×10^{-4}	(7)
1,1,1-Trichloroethane	155	(1)	1.7×10^{-2}	(8)
1,1,2-Trichloroethane	48	(3)	9.1×10^{-4}	(7)
Trichloroethene	106	(10)	9.7×10^{-3}	(10)
Trichlorofluoromethane (F-11)	479	(1)	6.0×10^{-2}	(2)
1,2,3-Trichloropropane	ND		ND	

TABLE 1 (continued)

Compound	K_{oc} (source) (mL/g)	K_H (source) (atm-m^3-mol^{-1})
Toluene	151 (10)	6.3×10^{-3} (2)
Vinyl acetate	17 (3)	3.8×10^{-4} (4)
Vinyl chloride	66 (3,9)	2.8×10^{-2} (8)
Xylene (o-xylene)	363 (1)	5.7×10^{-3} (2)

Sources:
1. Griffin and Roy [13].
2. Roy and Griffin [3].
3. Calculated using the regression of Hassett et al. [14].
4. Estimated from vapor pressure and solubility data.
5. Kenaga and Goring [15].
6. Nichoison et al. [16].
7. Nirmalakhandan and Speece [17].
8. Gossett [18].
9. Nirmalakhandan and Speece [19].
10. Garbarini and Lion [20].
ND, not determined.

A vertical extraction well results in radial flow patterns [2]. The volume of contaminated material was designed as a cylinder with radial flow towards the well (Fig. 1). The volume of air in the pore spaces (V_a) was calculated as

$$V_a = \pi r_e^2 Z (1 - \eta_l - (\rho_b/\rho_s)) \tag{11}$$

where Z is the length of the cylindrical volume, and ρ_s is particle density.

The accumulative volume of air passed through the cylinder (V_t) in eq. (7) was calculated as

$$V_t = Q Z_s t \tag{12}$$

where Q is the flow rate from eq. (10), Z_s is the length of the well open to air flow, and t is time.

Volatile organic compounds

The specific volatile organic compounds considered in this study are given in Table 1 and were those listed as the Appendix I chemicals by the U.S. EPA in the proposed Subtitle D regulations [21]. It was assumed that the liquid phase at the site model was water, and that Henry's law described the vapor-phase partitioning of the VOCs from the aqueous phase. A Henry's law constant (K_H) was compiled for each compound. It should be noted that modeling the extraction of free organic liquids may require the use of Raoult's Law to calculate vapor pressures, depending on the mole fraction of the organic component to be extracted (see ref. [22]). Adsorption constants for solid–liquid interactions were derived from soil organic carbon–water partition coefficients (K_{oc}) by the relation $K_d = K_{oc} \times \%$ organic carbon/100 [3]. It should be noted also that vapor-phase adsorption by dry materials was not considered in the derivation of the exponential removal model. It is generally recognized that

vapor phase adsorption by aquifer materials in the absence of water vapor is greater than from aqueous media [23–25]. With an increase in adsorbent water content, the adsorption of VOCs generally decreases due to competitive interactions with water molecules. The relative humidity of soil air is usually > 98% [26], and therefore adsorption constants derived from solid–liquid interactions (i.e., saturated conditions) may be reasonable first-order coefficients for vapor-phase adsorption from partially water-saturated soils [3]. The exponential removal model may overestimate the rate of VOC removal from relatively dry soil materials if solid–liquid adsorption constants are used.

Results

When computations were performed simulating the effects of a vacuum applied to the cylindrical site model under the conditions specified, the relative concentrations of most of the Appendix I compounds decreased rapidly (Fig. 2). The predicted rates of removal were initially rapid, followed by slower rates as the relative concentrations asymptotically approached zero. The general form of these predicted rate curves compared favorably to those from actual field applications of *in situ* extraction [1,2,27]. It has been hypothesized that the gradual decrease in the rate of VOC extraction is the result of diffusion-controlled processes. After the initial removal of organic vapors, the rate of mass transfer from immobile parcels of air and interstitial water may be limited by the rates of diffusion into the convective flow of air [2]. Cadena et al. [28] generalized that the volatilization of compounds with a Henry's law constant of 1.6×10^{-4} atm-m^3-mol^{-1} or greater is directly proportional to the water diffusion coefficient, and inversely proportional to the thickness of the film of water around the soil particle. The decrease in the rate of extraction of total VOC may also be due to a shift to less volatile substances after the selective removal of the more volatile constituents [1]. Field applications have also indicated that the removal rate may be interrupted, followed by "spikes" of increased concentrations in the air stream [10,27]. When the vacuum is turned off then restarted during the latter part of the extraction interval, spike yields have been detected (Fig. 2). This spiking phenomenon has been interpreted as the result of vapor diffusion from areas of lower permeability or areas beyond the radius of influence. Because of its simplicity, the exponential model does not predict the occurrence of such spikes.

The general extractability of the Appendix I compounds is given in Table 2. Under the site conditions imposed, the exponential removal model predicted that 85% or greater of the mass initially present of 23 VOCs would be removed after 100 days of continuous sweeping. The extractability of 10 of the chemicals could not be studied because of a lack of K_H and/or K_{oc} values. These simulations suggested that the rate of removal of relatively water-soluble compounds, such as alcohols and ketones, is extremely slow and may be impractical in field
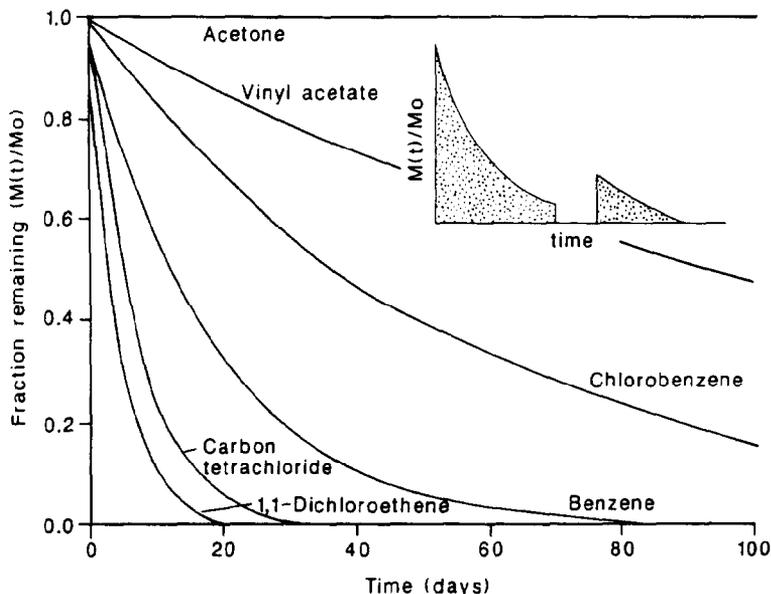
Fig. 2. Predicted removal curves of selected volatile organic compounds from the hypothetical site (Fig. 1) as a function of time. The insert (upper right) indicates the general behavior of the "spiking" phenomena discussed by Lisiecki and Payne [27]. The simulation conditions were $Z = 20$ m, $Z_s = 10$ m, $r_w = 0.2$ m, $r_e = 10$ m, $P_w = 0.9$ atm, $P_e = P_a = 1$ atm, $k = 1$ D, $\rho_s = 2.65$ g/cm^3, organic carbon $= 0.15\%$, and $\mu = 1.8 \times 10^{-2}$ mPa-s. The soil pores were assumed to be 50% saturated with water at a temperature of 20°C.

applications. For example, the predicted rates indicated that it would take about 77 years to remove 99% of the acetone initially present in the site. However, acetone and other ketones have been removed from contaminated sites in shorter time frames [27]. A possible mechanism to account for this apparent discrepancy may be that the more water-soluble compounds are entrained in the water vapor that is concomitantly withdrawn from the vadose zone. In the actual application of *in situ* extraction, an air–water separator may be placed in line between the extraction well and the blower [2]. This condensation is then collected for treatment and/or disposal. The simple screening model used in this study does not take into account the removal of VOCs by this mechanism, and thus it may yield conservative estimates of removal.

Hutzler et al. [2] suggested that compounds with a Henry law constant that is greater than approximately 2.4×10^{-4} atm-m^3-mol^{-1} are likely candidates for *in situ* extraction. Simulations using the exponential removal model suggested that if the compound is not strongly adsorbed (i.e., $K_{oc} < 100$ mL/g, then compounds with a Henry law constant of approximately 10^{-4} atm-m^3-mol^{-1} and greater are favored (Fig. 3). With an increase in K_{oc}, a corresponding decrease occurred in the rate of extration. Values for 25 of the Appendix I compounds were less than 100 mL/g (Table 1), which would explain in part

TABLE 2

Relative extractabilities of the Appendix I VOCs. Conditions for extraction for the site model given in Fig. 1 and simulation parameters given in Fig. 2

Compound	Removal after 100 days (%)	Time to remove 99% (days)
Acetone	2	28,000
Acrolein	17	2,600
Acrylonitrile	18	2,400
Benzene	100	76
Bromoform	45	770
Bromomethane	100	46
2-Butanone (methyl ethyl ketone)	5	8,300
Carbon disulfide	15	2,800
Carbon tetrachloride	100	32
Chlorobenzene	85	250
Chloroethane	100	33
Chloroform	100	79
Chloromethane	100	35
Dibromomethane	80	290
Dichlorodifluoromethane (F-12)	100	10
1,1-Dichloroethane	100	58
1,2-Dichloroethane	88	220
1,1-Dichloroethene	100	20
trans-1,2-Dichloroethene	100	68
cis-1,3-Dichloropropene	98	110
trans-1,3-Dichloropropene	96	150
Ethanol	2	31,000
Ethylbenzene	91	195
2-Hexanone	2	30,000
Methylene chloride	100	84
4-Methyl-2-pentanone	22	1,900
Styrene	13	3,500
1,1,2,2-Tetrachloroethane	42	860
1,1,1-Trichloroethane	100	39
1,1,2-Trichloroethane	74	340
Trichloroethene	100	64
Trichlorofluoromethane (F-11)	100	29
Toluene	99	95
Vinyl acetate	53	610
Vinyl chloride	100	20
Xylene (o-xylene)	91	190

the apparent extractability of these chemicals. Adsorption of individual components depends not only on their respective K_{oc} values, but also on the amount of organic matter in the subsurface. If all other parameters are held constant, an increase in organic carbon content resulted in decreased rates of removal
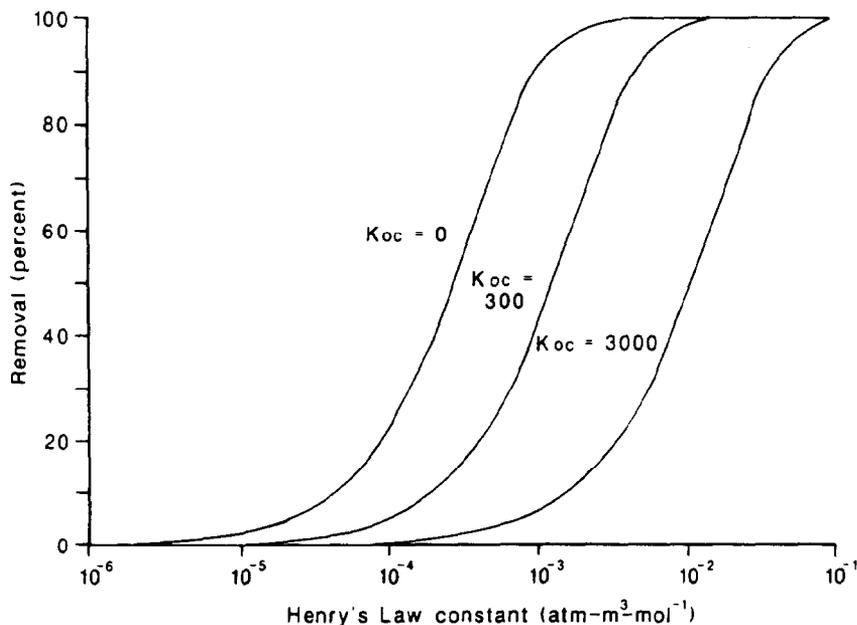
Fig. 3. Predicted removal curves of volatile organic compounds as a function of the Henry's law constant (K_H), and organic carbon-water partition coefficient (K_{oc}, mL/g) after 100 days of continuous extraction. The simulation conditions were the same as those in Fig. 2.

(Fig. 4). Volatile organic chemicals with K_{oc} values that were greater than about 100 mL/g were particularly sensitive to soil organic carbon content within a relatively narrow range of 0 to 0.4%.

The air permeability of a particular site will control the rate of air movement and therefore the rate of VOC removal [2]. Simulated rates of removal indicated that air permeability may be a critical parameter (Fig. 5). Field experience has demonstrated that *in situ* extraction is more likely to be successful when applied to highly permeable materials [2]. The relative extractabilities of the Appendix I compounds (Table 2) were based on air permeability of 1 darcy (D). In the range of air permeabilities associated with silt-sized grains, the modeling results indicated that as *k* decreases, the rates of extraction of all of the Appendix I compounds were reduced (Fig. 5). At air permeabilities less than 10 mD, the predicted removal curves suggested that *in situ* extraction may not be feasible for some compounds under these conditions because of the inability of air to sweep through relatively impermeable, homogenous material in sufficient volume to be practical. Vapor extraction has been successfully used at sites that contained clay lenses or thin silt layers. In some situations, VOCs were able to diffuse from the less permeable zones into more permeable layers (J.S. Gierke and N.J. Hutzler, 1989, Michigan Technological University, personal communication).
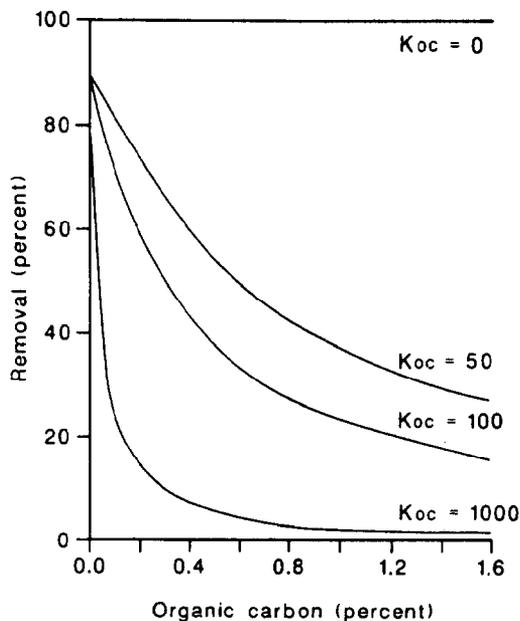
Fig. 4. Predicted removal curves of volatile organic compounds as a function of organic carbon content and the organic carbon–water partition coefficient (K_{oc}) after 100 days of continuous extraction. K_H was held constant as 10^{-3} atm-m^3-mol^{-1}. The other simulation conditions were the same as those in Fig. 2.
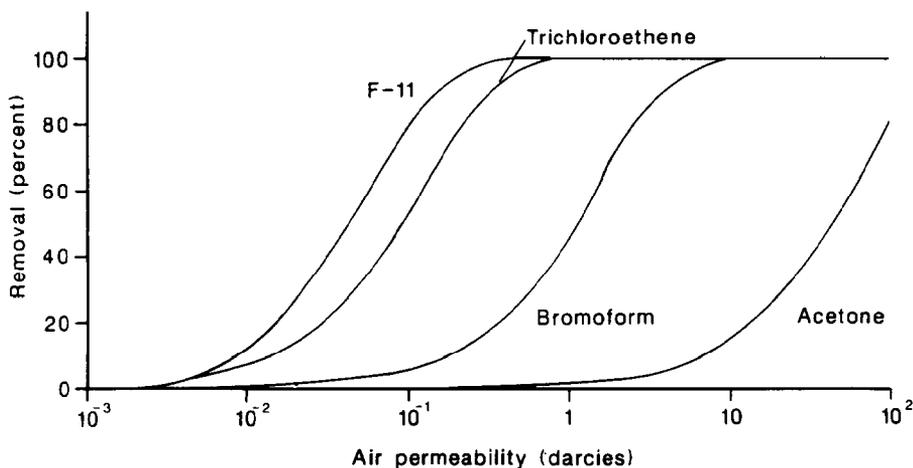

Fig. 5. Predicted removal curves of selected volatile organic compounds as a function of air permeability after 100 days of continuous extraction. The other simulation conditions were the same as those in Fig. 2.

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Given that the physicochemical characteristics of the specific site cannot be changed to facilitate *in situ* extraction, it may be helpful to examine the influences of the extraction well parameters. In the previous simulation, the air pressure in the well was held constant at 0.9 atm. If all of the other variables are held constant, a decrease in the atmospheric pressure in the extraction well resulted in enhanced rates of removal (Fig. 6) because of the increased volume of air passing through the contaminated material. However, in this specific system, modeling had indicated that a partial vacuum of 0.9 atm was sufficient to remove most of the Appendix I VOCs after 100 days of operation. Consequently, an increase in the pressure gradient would not be necessary. A decrease in air pressure in the well resulted in enhanced rates of extraction of the relatively resistant chemicals such as ethanol, but it was problematic whether these enhanced rates were truly significant. Hutzler et al. [2] generalized that higher flow rates tend to increase vapor removal because the radius of influence expands. In Fig. 6, the radius of influence was held constant; therefore, an increase in the pressure gradient may result in larger quantities of VOC removed, but it may not necessarily have a dramatic effect on the rate of removal. In one case study, the rate of VOC extraction had to be reduced because of concerns about atmospheric emissions of the extracted vapors [3].
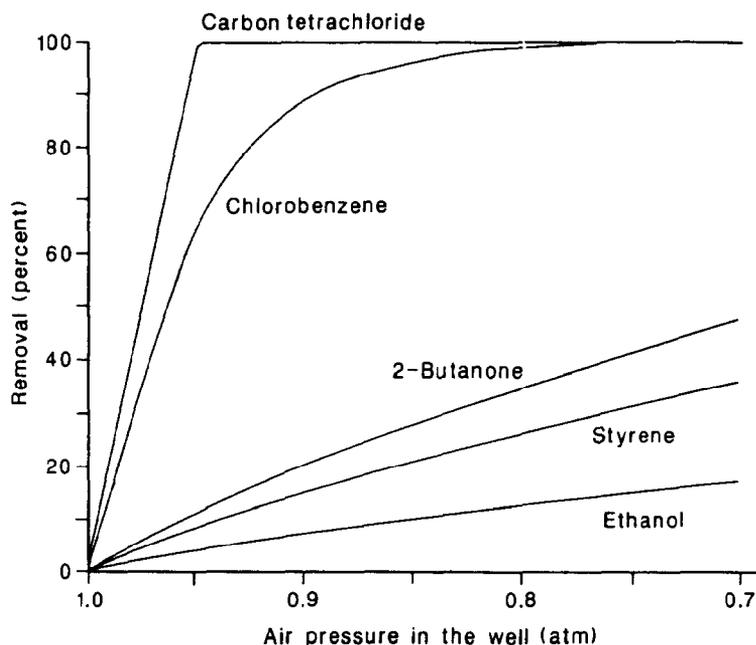

Fig. 6. Predicted removal curves of selected volatile organic compounds as a function of the air pressure in the extraction well after 100 days of continuous extraction from a soil volume that is 10% saturated with water. The other simulation conditions were the same as those in Fig. 2.

Varying the size of the extraction well is another possible method of regulating air flow. However, simulations suggested that the radius of an individual well had little effect on the rates of extraction (not shown). The rate of extraction was found to be more sensitive to the length of the screened interval (Z_s). Inspection of eq. (12) indicates that the flow rate is directly proportional to the interval of the well that is open. When the model was applied to a less permeable soil volume ($k=0.1$ D), enhanced rates of removal were associated with an increase in Z_s (Fig. 7), although the impact on less extractable compounds such as styrene was minimal. However, laboratory-scale studies and field experiences summarized by Hutzler et al. [2] suggested that some portion of the well between the top of the screen and the surface needs to be constructed with solid pipe and sealed to prevent the short circuiting of air from the atmosphere. Short circuiting would slow rates of extraction, and its effects cannot be predicted using the exponential-removal model.

Very few extraction data were available to illustrate the use of the exponential removal model. Hutzler et al. [2] described a laboratory study conducted by AWARE, Inc., where a vacuum was applied to soil columns to remove VOCs. Air was drawn through one column at a rate of approximately 3.5 cm^3/min for 11 days. The amount of VOC removal was then analytically determined. The
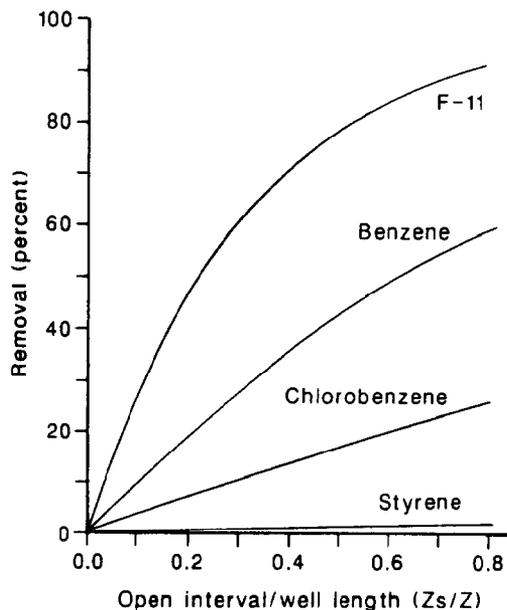

Fig. 7. Predicted removal curves of selected volatile organic compounds as a function of the ratio of screened well length to the total of the well after 100 days of continuous extraction. The soil volume was assumed to be 50% water saturated and $k=0.1$ D. The other simulation conditions were the same as those in Fig. 2.

TABLE 3

Comparison of observed extractability with those predicted by the concepts of the exponential removal model

Compound	Amount removed				
	Observed (%)	Predicted (%)			
Ethylbenzene	45	55			
Toluene	73	90			
O-xylene	64	59			
Measured parameters			Assumed parameters		
Organic matter content (%)	4.4%		Organic carbon[a] (%)	2.59	
Total porosity =	0.54		ρ_b (g/cm^3)	1.6	
Moisture content =	16%		ρ_s (g/cm^3)	2.65	
Column length (m)	0.3		Temperature (°C)	25	
Column radius (m)	0.032				

[a]Assuming that % organic carbon = 0.59% organic matter [29].

predicted amounts of VOC removal were calculated using the parameters that were measured coupled with four assumed values as given in Table 3. After 11 days of extraction, the predicted reductions were in good agreement with those observed.

Conclusions

A simple extraction model was applied to describe the *in situ* removal of volatile organic compounds from the vadose zone. This model can be used as a screening tool for conducting sensitivity analyses. In the derivation of the model, it was assumed that the total mass of contaminant exists in three forms: as vapors, in interstitial liquids, and as adsorbed phases. The equilibrium relationships between these three phases were disrupted when air was swept through a hypothetical site which in turn resulted in the gradual removal of the volatile organic compounds listed in Appendix I. Most of the Appendix I compounds appeared to be extractable by this technique when the liquid phase is water although modeling results suggested that the rates of extracting ketones and alcohols may be very slow. Ten of the Appendix I compounds could not be evaluated because of a lack of Henry's law constants (K_H) and/or soil organic carbon–water partition coefficients (K_{oc}).

In general, the rates of extracting compounds that were not strongly adsorbed ($K_{oc} < 100$ mL/g) were significantly greater when K_H was equal to or greater than 10^{-4} atm-m^3-mol^{-1} when K_{oc} was greater than approximately 100

mL/g, the rates of extraction were particularly sensitive to the amount of organic carbon present to the vadose zone.

The permeability of the porous material to air (k) was a critical factor in relation to VOC removal rates; rates were slower as k was reduced. *In situ* extraction should be evaluated carefully when applied to site remediation when k is less than 10 mD. In highly permeable materials where k was greater than 10 D, VOC removal rates were not sensitive to greater k and were less sensitive to K_H, or K_{oc}. A decrease in the atmospheric pressure in a single extraction well at the site model resulted in accelerated rates of extraction, but did not significantly influence the overall removal trends of the Appendix I VOCs. Also, the diameter of a single well had little effect on rates of removal. In contrast, an increase in the length of the well that is open to the contaminated zone may be an important consideration, especially for relatively impermeable materials.

Acknowledgments

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