More Realistic Soil Cleanup Standards with Dual-Equilibrium Desorption

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Abstract

The desorption of contaminants from soils/sediments is one of the most important processes controlling contaminant transport and environmental risks. None of the currently adopted desorption models can accurately quantify desorption at relatively low concentrations; these models often overestimate the desorption and thus the risks of hydrophobic organic chemicals, such as benzene and chlorinated solvents. In reality, desorption is generally found to be biphasic, with two soil-phase compartments. A new dual-equilibrium desorption (DED) model has been developed to account for the biphasic desorption. This model has been tested using a wide range of laboratory and field data and has been used to explain key observations related to underground storage tank plumes. The DED model relates the amount of a chemical sorbed to the aqueous concentration, with simple parameters including octanol-water partition coefficient, solubility, and fractional organic carbon; thus, it is the only biphasic model, to date, that is based on readily available parameters. The DED model can be easily incorporated into standard risk and transport models. According to this model, many regulatory standards of soils and sediments could be increased without increasing the risks.

Introduction

Soil contamination problems are particularly difficult due to the large volumes of soils that may require treatment. While small areas of highly contaminated soils can be found near direct sources of pollutant discharge, or at the point of a spill, large areas of contaminated soil with low pollutant concentrations represent the most significant costs and difficulties for treatment. For instance, it was reported that for the underground storage tank (UST) program alone, there were 160,000 sites in 2000 with confirmed releases where cleanup of contaminated soils had not yet been completed. Assuming that cleanup of contaminated soils under a risk-based program averages $24,000 per site (e.g., as reported by the State of Texas in ASTM 1995), and that 50% of these sites will require soil cleanup, the total liability may approach nearly $1.5 billion for the UST program alone.

Contaminated soils pose ecological and human-health risks through various pathways, of which the leaching of contaminants from soils to ground water is often the most predominant. For example, the ASTM risk-based corrective action (RBCA) (ASTM 1995; Newell and Connor 1998) standard assumes contaminants leach from unsaturated soils into ground water, thereby creating a dissolved plume when the percolating water mixes with clean ground water in the underlying aquifer. Human exposure may occur through drinking the ground water from the aquifer, therefore causing risk. Many programs under which soil contamination is regulated (e.g., CERCLA, RCRA, UST programs) use a risk-based approach to derive soil regulatory standards. For the soil-to-ground water pathway, the soil standards are derived from ground water standards using simple partitioning and dilution models. All of these models assume that sorption and desorption are similar processes and that the partition coefficients determined through sorption experiments are also applicable to desorption. Such leaching models are currently used by moret than 30 states for at least one state regulatory program, and are commonly used for many EPA-supervised RCRA and CERCLA risk assessments.

In reality, the leaching of contaminants from soils to ground water often cannot be modeled accurately with these simplified models. Indeed, numerous studies have shown that at low concentrations, desorption is very difficult and contaminants in this region persist much longer than would be expected from conventional physical-chemical and biodegradation parameters (Linz and Nakles 1997). If this persistent fraction is actually a general characteristic of the soil-hydrocarbon interaction, as has been shown at Rice University for a number of soil-chemical combinations (Fu et al. 1994; Kan et al. 1994; Hunter et al. 1996; Kan et al. 1997a; Kan et al. 1998; Chen et al. 1999; Chen et al. 2000a; Chen et al. 2000c), and hydrocarbons sorbed in this manner are not available as expected, then it might be possible to reestablish acceptable environmental screening levels, or end points, that will result in enormous cost savings but little or no increase in ecological and human-health risks to soil ecosystems, because the desorption/water transport path will be greatly reduced (Kan et al. 1998; Chen et al. 2000b). (See later section titled "Impact of Dual-Equilibrium Desorption on Soil Leaching Models.")

Thus far, numerous theories and models have been used to express the general notion that sorption and desorption of soil contaminants are often different processes, including slow desorption, bound contaminant, hysteresis, irreversible sorption, amorphous and glassy sorption phases, to mention a few (Di Toro and Horzempa 1982; Ball and Roberts 1991; Connaughton et al. 1993; Carroll et al. 1994;

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Burgos et al. 1996; Valsaraj et al. 1997; Chiou and Kile 1998; Huang and Weber 1998; Pignatello 1998; Xing and Pignatello 1998; Gilltette et al. 1999; Alexander 2000; Stroo et al. 2000). Unfortunately, these theories require extensive experimentation for every soil/compound combination, which is impractical. However, all of these interpretations have proposed the existence of two distinct sorption and desorption processes, one process related to sorption and desorption at high contaminant concentrations and a second process at low concentrations, predominantly observed during desorption. Desorption is typically characterized by the observation that, after a period of weathering, aqueous contaminant concentrations are often so low that if regulators were certain that the concentrations would not increase nor become bio-available in the future, then the soils would be of little ecological and human-health concern.

In this paper a new unified model of contaminant sorption and desorption is presented, called the "dual-equilibrium desorption" (DED) model. This model is based on several years of research on the mechanism(s) of contaminant interactions with soils and sediments by the authors and numerous laboratory and field reports from other groups on a diverse range of organic compounds, sediments, soils, and conditions (Fu et al. 1994; Kan et al. 1994; Kan et al. 1997a; Kan et al. 1998; Chen et al. 1999; Kan et al. 1999; Chen et al. 2000a; Chen et al. 2000c). The primary advantage of the DED model is that the only compound-specific parameters needed are the octanol-water partition coefficient, K_{ow}, and solubility. At present, it is the only model available that can describe the commonly observed bimodal nature of contaminant desorption from soils and sediments using known parameters. This paper presents a short review of the principal theories and observations incorporated into the DED model; discusses the equations and several laboratory and field examples supporting this model; and proposes a quantitative application of the new model to current environmental problems and cleanup standards.

Background and Theory

Many research groups have studied the sorption and desorption of organic chemicals in soils, sediments, and aquifer materials both in the laboratory and in the field (Wu and Gschwend 1986; Brusseau and Rao 1989; Ball and Roberts 1991; Weber et al. 1992; Carroll et al. 1994; Burgos et al. 1996; Pignatello and Xing 1996; Chiou and Kile 1998; Kan et al. 1998). Several common observations have emerged from these studies and are included in the model presented. The following is a brief qualitative summary of the key observations.

1. Sorption and desorption are both biphasic, consisting of two compartments, each with unique equilibrium and kinetic characteristics (Carroll et al. 1994; Pignatello and Xing 1996; Weber and Huang 1996). The nature of the two compartments has not yet been identified; however, most of the researchers consider the two compartments as different types of sediment organic matrices, e.g., amorphous (flexible, expanded) versus glassy (rigid, dense) organic matters (Pignatello and Xing 1996; Weber and Huang 1996), soil organic matter versus high-affinity materials (Chiou and Kile 1998), and adsorption to sediment surface versus entrapment in sediment pores (Adamson 1990; Farrell and Reinhard 1994).
2. Partitioning to and from the first compartment generally accounts for the bulk of contaminant sorption, depending on the initial concentration. At high initial source zone concentrations (aqueous or solid phase) most of the sorbed contaminant may be associated with the first compartment (85% to 99.9 +%), but at low exposures, 50% or less of the contaminant may be sorbed in the first compartment (Kan et al. 1998). The soil/water partition coefficient for the first compartment is proportional to the fraction of organic carbon, f_{OC}, and to the organic carbon normalized partition coefficient, K_{OC}^{1st} [(mg of contaminant sorbed in first compartment/kg of soil organic carbon)/(mg of contaminant/liter of solution)] (Karickhoff et al. 1979; Schwarzenbach et al. 1993) for a discussion of these relationships); this K_{OC}^{1st} is the quantity that is presently used in most models and regulations (TNRCC 1999). In practice, sorption to the first compartment is typically found to be linear over a wide range of concentration from trace levels to near the aqueous solubility, i.e., no distinct sorption maximum is typically found below the aqueous solubility. In addition, the rate of both sorption and desorption to and from the first compartment is generally rapid compared to ground water flow and can be described using common kinetic expressions, such as the radial diffusion model (Wu and Gschwend 1986).
3. Sorption and desorption to and from the second compartment is distinctly different from that of the first compartment in, at least, four well characterized ways (Kan et al. 1997a; Kan et al. 1998). First, the second compartment has a well-defined maximum sorption capacity, q_{max}^{2nd} (maximum mg of contaminant sorbed in second compartment/kg of soil), which is proportional to f_{OC}, and secondarily to compound-specific constants (equations given later). Second, for all hydrophobic organic compounds partitioning to this second compartment is characterized by a single organic-carbon normalized partition coefficient, K_{OC}^{2nd} [(mg of contaminant sorbed in second compartment/kg of soil organic carbon)/(mg of contaminant/liter of solution)]. A summary of extensive laboratory and field data used to establish this aspect will be presented in the results section. Third, even when very low aqueous concentrations are added to soil or sediment, only about one-third to one-half of the amount sorbed will be associated with the second compartment. In fact, the second compartment can be saturated to the same q_{max}^{2nd} value in one single exposure of high aqueous concentration or via several successive exposures at lower concentrations; i.e., at a given sorption condition only a fraction (referred to as "f" in the text) of q_{max}^{2nd} will be filled (Kan et al. 1997a). This third property is probably the source of the often-observed "sorption hysteresis" in the field and the laboratory and may be the prime source of disagreement between laboratory researchers and field engineers trying to model the same system. Fourth, the sorption kinetics of this second compartment are generally slower than the first. The characteristic sorption and desorption time is about one to seven days, and appears to be approximated by the standard radial diffusion model with K_{OC}^{2nd} used in the radial diffusion equation instead of K_{OC}^{1st} (Kan et al. 1999).
4. The impacts of cosolvents (methanol, isopropanol, acetone, etc.), surfactants, and mobile colloids on contaminant sorption and desorption is to alter the effective aqueous phase "activity," or concentration, and these effects are thereby predictable (Schwarzenbach et al. 1993; Kan et al. 1997b).
5. Contaminants sorbed in the second compartment are not available for reactions (Alexander 2000), but once desorbed they can undergo chemical and biological reactions as expected from the aqueous concentration and solution conditions (Kan et al. 1998).

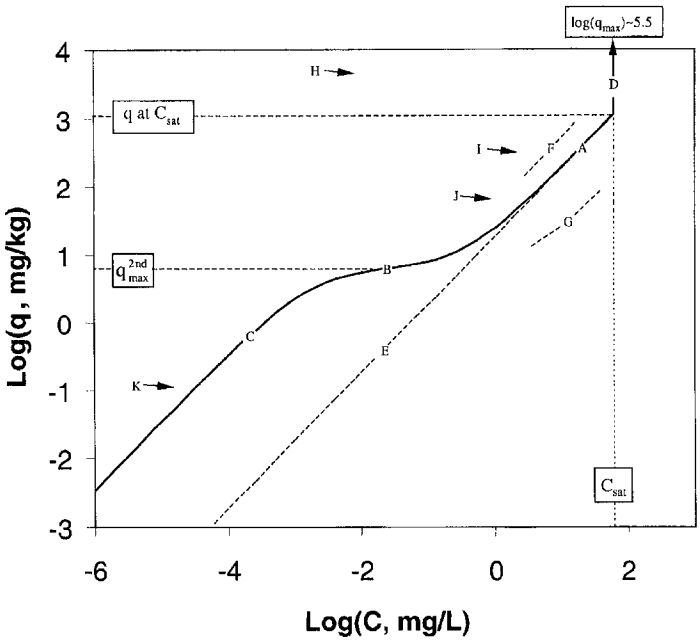

Figure 1. Example isotherm plot of log (q, mg/kg-solid) versus log (C_{aq}, mg/L) for 1,4-dichlorobenzene (1,4-DCB) in soil or sediment with f_{OC} = 0.01. C_{sat}. = 80 mg/L for 1,4-DCB. See text for more complete discussion of lettered curves. The solid curve, A/B/C, is the expected dual-equilibrium desorption curve. The lettered curves correspond to: D (free phase equilibrium); E (linear equilibrium); F (presence of NAPL); and G (presence of cosolvent, surfactant, or colloid). Curve G will follow the solid isotherm curves, A/B/C, but displaced to the right as determined by the amount of cosolvent, etc., in solution. Points H, I, J, and K correspond to nonequilibrium kinetic desorption. The slope of each nonequilibrium point toward the isotherm is the same (slope = $-V_w/ms$, where V_w is the water volume and m_s is the solid mass).

The DED model can account for all of the previous observations and can be readily incorporated into common transport and risk models and equations. In addition, all of the necessary constants are readily calculated from commonly available parameters; this is an important aspect that is not presently available for any other general theory of sorption and desorption.

In the DED model, sorption is assumed to be a linear combination of the first and second compartments:

$$q = q^{1st} + q^{2nd} \tag{1}$$

where q (mg/kg soil) represents total sorption; q^{1st} and q^{2nd} (mg/kg soil); represent sorption to the first and second compartments, respectively:

$$q^{1st} = K_{OC}^{1st} \cdot f_{OC} \cdot C \tag{2}$$

where C (mg/L) is the aqueous concentration of the contaminant. All of the observed features of the second compartment, that are listed previously, can be described by a Langmuir-type isotherm if the value of q_{max}^{2nd} is multiplied by a factor, f, to represent the fraction of the second compartment that is saturated upon exposure:

$$q^{2nd} = \frac{K_{OC}^{2nd} \cdot f_{OC} \cdot f \cdot q_{max}^{2nd} \cdot C}{f \cdot q_{max}^{2nd} + K_{OC}^{2nd} \cdot f_{OC} \cdot C} \tag{3}$$

It has been shown for field systems that assigning a value of f = 1 is reasonable (Kan et al. 1998). A value of f = 1 will always yield a conservative estimate of q. Combining Equations 1, 2, and 3 and assuming f = 1, the general DED isotherm model becomes (Kan et al. 1998)

$$q = K_{OC}^{1st} \cdot f_{OC} \cdot C + \frac{K_{OC}^{2nd} \cdot f_{OC} \cdot q_{max}^{2nd} \cdot C}{q_{max}^{2nd} + K_{OC}^{2nd} \cdot f_{OC} \cdot C} \tag{4}$$

At low aqueous concentrations Equation 4 reduces to a linear isotherm, $q = K_{OC}^{2nd} \cdot f_{OC} \cdot C$, assuming, as is typical, that $K_{OC}^{1st} < K_{OC}^{2nd}$. Equation 4 is illustrated in Figure 1 by curves A/B/C for 1,4-dichlorobenzene (1,4-DCB) with f_{OC} = 0.01. As in the figure, at low concentrations desorption deviated significantly from the conventional linear isotherm that is described by curve E.

Although Equations 1 and 4 are probably the most widely applicable, there are situations where Equations 1 and 4 need to be modified to describe other specific processes. Several of these additional processes are illustrated in Figure 1 along with Equation 4:

- **Free phase contaminant**. If there is an equilibrium with a free phase of the contaminant, then $q^{FreePhase} = (\theta_{FP}\rho_{FP}/\rho_b)10^6$ mg/kg, where θ_{FP} is the volume fraction in the porous medium containing free phase contaminant, ρ_{FP} is the free phase density, ρ_b is the soil bulk density; the maximum value for $q^{FreePhase}$ occurs when θ_{FP} is equal to the total porosity (curve D).
- **Presence of NAPL/TPH**. When nonaqueous phase liquids (NAPL), such as total petroleum hydrocarbon (TPH) liquids, are present, contaminants also partition into the NAPL phase. Thus, the total amount of sorption (i.e., the total concentrations in soil, which includes both the amount adsorbed to soil as well as the amount partitioning into NAPL) increases. For example, the sorption to TPH can be expressed as $q^{TPH} = K_{TPH}\rho_{TPH}^{-1} f_{TPH} C$, where K_{TPH} (L/L-TPH) is the contaminant partition constant to the TPH liquid phase, ρ_{TPH} is TPH density, and f_{TPH} is the wt/wt fraction of TPH in the porous medium (curve F).
- **Colloid, surfactant, cosolvent—enhanced solubility.**
  1. If substantial mobile colloids are present in the water, then each C-term in Equation 4 must be replaced by $C = C_w/(1 + K_C \cdot r_{cw})$, where C_w (mg/L) is the total contaminant concentration (free plus colloidally complexed) in solution, K_C (L/kg-colloid) is the partition constant to the aqueous colloids, and r_{cw} (kg-colloid/L) is the ratio of the mass of colloid to volume of solution (curve G).
  2. If surfactants are present in solution above the critical micelle concentration (cmc) for the surfactant, then the "C" terms in Equation 4 should be replaced by $C = C_w/(1 + K_{surf} \cdot r_{surf/w})$, where $r_{surf/w}$(kg-surf/L) refers to the mass of surfactant in the micellular form per liter of solution, and K_{surf} (L/kg-surf) is the partition coefficient to the surfactant—generally found to be of similar magnitude as K_{OC}^{1st} (also represented by curve G).
  3. If cosolvents such as methanol, isopropanol, acetone, and others are in solution, the K_{OC}^{1st} and K_{OC}^{2nd} terms in Equations 1 and 4 must be corrected to their respective values for cosolvents instead of water. This correction can be done in several ways (Schwarzenbach et al. 1993). One method is to multiply both constants by the ratio: $\gamma_{cosolv}\mathbf{V}_{cosolv}/\gamma_w\mathbf{V}_w$, where $\mathbf{V}_{cosolv}$ and $\mathbf{V}_w$ (L/mole) are the solvent molar volumes and γ_{cosolv} and γ_w represent the con-

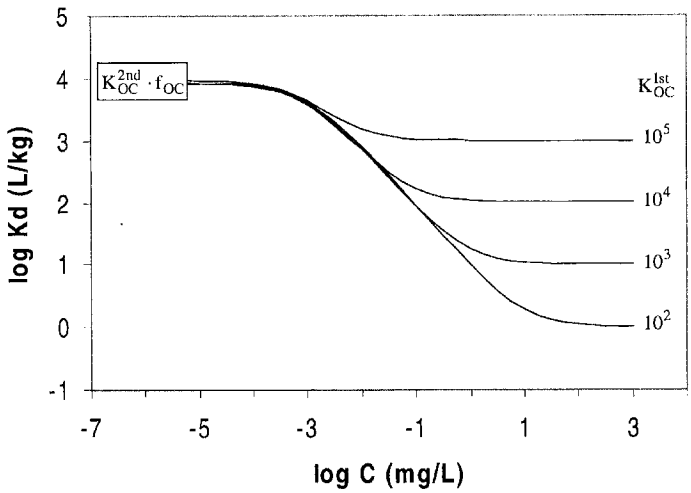

Figure 2. Plot of distribution coefficient (K_d) versus the aqueous concentrations, C. The solid curves are calculated for K_{OC}^{1st} values from 10^2 to 10^5. The fractional organic carbon content (f_{oc}) is assumed to be 0.01 and K_{OC}^{2nd} is equal to $10^{5.92}$ in all cases.

taminant fugacity coefficients in water and cosolvent, which can be readily calculated by several UNIFAC programs (Banerjee 1985; Hansen et al. 1991; Kan and Tomson 1996) (also represented by curve G).

Returning to Equation 4, the value of K_{OC}^{1st} can be obtained from numerous tabulations, specific correlations, and explicit measurement. The following equation has been found to work well for many groups of hydrophobic organic chemicals (Karickhoff et al. 1979):

$$K_{OC}^{1st} = 0.63K_{ow} \tag{5}$$

K_{ow} can be found in several standard reference tables for most common compounds (Leo et al. 1971). Numerous other correlations (Lyman et al. 1982; Ball and Roberts 1991; Schwarzenbach et al. 1993) can be used to estimate, K_{OC}^{1st}, e.g.,

$$\log = K_{OC}^{1st}\, 0.82 \cdot \log K_{ow} + 0.44$$

The value of K_{OC}^{2nd} has been found (see "Results" for a summary) to be a single constant for all hydrophobic compounds tested to date. Combining laboratory and field data together for a wide range of compounds and conditions:

$$\log K_{OC}^{2nd} = 5.92 \pm 0.16, \qquad n = 41 \tag{6}$$

Several explanations have been advanced to account for this observation (Kan et al. 1998; Chen et al. 2000c). One possibility is that chemicals in the second compartment form an organic complex with soil organic matters (Schulten 1995; Schulten and Schnitzer 1997; Devitt and Wiesner 1998) so that the nature of adsorbents is masked by that of the complex.

Finally, the last term in Equation 4, q_{max}^{2nd}, can be either measured or calculated with the following equation:

$$q_{max}^{2nd} = f_{OC}\,\{K_{ow}\, C_{sat}\,(\text{mg/L})\}^{0.534} \tag{7}$$

where C_{sat} (mg/L) is the aqueous solubility (Kan et al. 1998; Chen 1999; Chen et al. 2000b). With Equations 5 to 7 all the terms in the sorption/desorption isotherm can be calculated.

In most partitioning models, the critical parameter to characterize sorption and desorption is the distribution coefficient, K_d (L/kg), defined as

$$K_d = \frac{q}{C} \tag{8}$$

Using Equation 4, this becomes

$$K_d = K_{OC}^{1st} \cdot f_{OC} + \frac{K_{OC}^{2nd} \cdot f_{OC} \cdot q_{max}^{2nd}}{q_{max}^{2nd} + K_{OC}^{2nd} \cdot f_{OC} \cdot C} \tag{9}$$

The concentration dependence of K_d at various K_{OC}^{1st} values is illustrated in Figure 2, each at $f_{OC} = 0.01$. As in the figure, the apparent K_d values gradually increase to the same $K_{OC}^{2nd} \cdot f_{OC}$value as C decreases, regardless of the K_{OC}^{1st} value.

An illustration of the direct use of these equations can be obtained from the one-dimensional advective-dispersion equation:

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - \lambda C \tag{10}$$

where D (m^2/s) is the dispersion coefficient, x (m) is distance in the x-direction, v (m/s) is the seepage velocity, λ (s^{-1}) is the first order rate constant for decay or reaction, and R is the retardation factor:

$$R = 1 + \frac{\rho_b}{\theta}\frac{dq}{dC} \tag{11}$$

with θ representing the porosity. When C is relatively large, the first compartment dominates the isotherm (curve A, Figure 1) and the retardation, Equation 11, becomes

$$R^{1st} = 1 + \frac{\rho_b}{\theta} K_{OC}^{1st} \cdot f_{OC} \tag{12}$$

When C is relatively small, the second compartment predominates the isotherm (curve C, Figure 1) and the retardation, Equation 11, becomes

$$R^{2nd} = 1 + \frac{\rho_b}{\theta} K_{OC}^{2nd} \cdot f_{OC} \tag{13}$$

Finally, the overall retardation equation using the DED isotherm, Equation 4, is given by

$$R = 1 + \frac{\rho_b}{\theta}\left(K_{OC}^{1st} \cdot f_{OC} + \frac{K_{OC}^{2nd} f_{OC} (q_{max}^{2nd})^2}{(q_{max}^{2nd} + K_{OC}^{2nd} f_{OC} C)^2}\right) \tag{14}$$

which is a function of the aqueous contaminant concentration, C, only in the transition region where $q \approx q_{max}^{2nd}$. Equation 14 can be readily modified to account for the effects of each of the additional possible aspects such as total petroleum hydrocarbons (TPH), colloids, etc. Because the amount of free phase is a function of how much was added by the spill, etc., the amount of free phase present is not a unique function of C and therefore the isotherm cannot be differentiated explicitly.

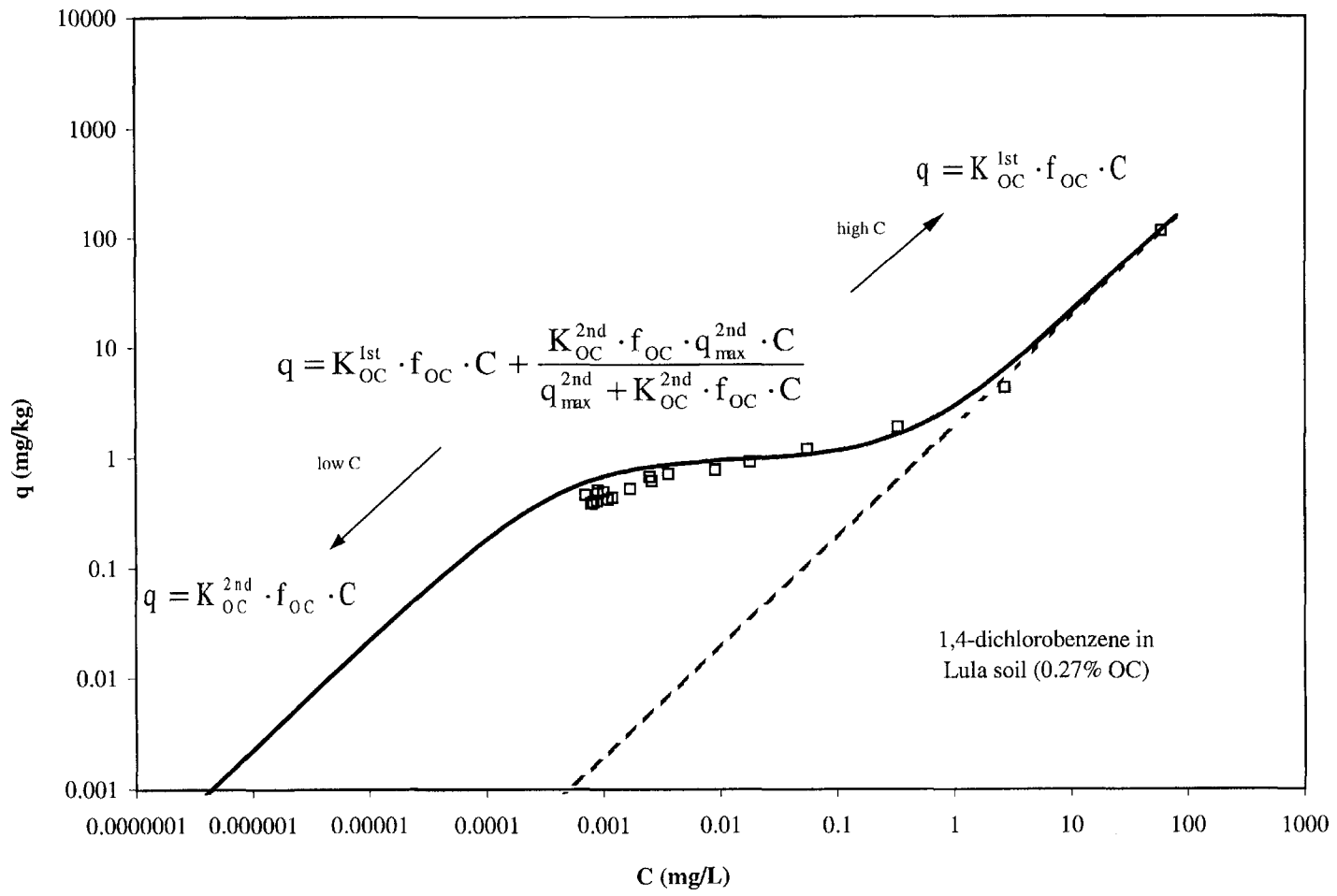

Figure 3. Plot of solid-phase concentration versus the aqueous phase concentration of model prediction and laboratory observations. Solid curve is the expected dual-equilibrium desorption curve, and the dashed line is the expected linear desorption curve. The solid curve is calculated with $K_{OC}^{1st} = 724$, $K_{OC}^{2nd} = 10^{5.92}$, and $q_{max}^{2nd} = 0.97$ mg/Kg; the data points are experimental desorption results of 1,4-dichlorobenzene from Lula soil (Chen et al. 2000a).

Table 1

Comparison of Field-Observed Sediment and Pore Water Concentrations of PAHs and PCBs in Boston Harbor versus DED Isotherm Predictions

Compound and Properties				Field Measurements				Isotherm Predictions	
Comp.	[a]$\log K_{ow}$	[b]$\log K_{OC}^{1st}$ L/kg-OC	Core Numbers	f_{OC} wt/wt	q/f_{OC} mg/kg-OC	C mg/L $\times 10^{+6}$	[c]$\log K_{OC}^{app}$ L/kg-OC	[d]C, Linear mg/L $\times 10^{+6}$	[e]C, DED mg/L $\times 10^{+6}$
Phenanthrene	4.57	4.37	1	0.052	30	17	6.25	1500	39
			2	0.055	36	7.1	6.70	1800	47
			3	0.033	34	8.6	6.60	1703	45
Pyrene	5.13	4.93	1	0.052	121	220	5.74	800	252
			2	0.055	87	84	6.02	550	147
			3	0.033	109	21	6.72	642	211
Cl_5PCB	6.36	6.16	1	0.052	0.63	0.44	6.15	0.87	0.28
			2	0.055	2.10	1.3	6.21	2.9	0.91
			3	0.033	0.68	0.56	6.08	0.94	0.31
Cl_6PCB	7.00	6.80	1	0.052	0.71	0.43	6.22	0.49	0.10
			2	0.055	2.46	1.00	6.39	1.7	0.34
			3	0.033	0.84	0.59	6.15	0.58	0.12

[a]Schwarzenbach et al. (1992)
[b]From Equation 5 in text
[c]$K_{OC}^{app} = q/(C \cdot f_{oc})$
[d]From Equation 2 in text
[e]DED value obtained by using q from column 6 and solving Equation 4 using Excel Goal Seek.
Field data were obtained from McGroddy et al. (1996).

Table 2
Comparison of Field-Observed Sediment and Pore Water Concentrations of Chlorinated Hydrocarbons from Bayou d'Inde versus DED Isotherm Predictions

Compound and Properties			Field Measurements			Isotherm Predictions	
[a]Compound	[b]$\log K_{ow}$	[c]$\log K_{OC}^{1st}$ L/kg-OC	q mg/kg	C mg/L × 10^{+6}	[d]$\log K_{OC}^{app}$ L/kg-OC	C, [e]Linear mg/L × 10^{+6}	C, [f]DED mg/L × 10^{+6}
1,2-DCB	3.49	3.29	0.291	9.0	5.90	360	8.1
1,3-DCB	3.50	3.30	4.14	48	6.32	51,000	137
1,4-DCB	3.47	3.27	3.36	74	6.04	44,000	114
1,2,3-TCB	4.14	3.94	0.394	12	5.90	1100	12.3
1,2,4-TCB	4.02	3.82	12.5	40	6.88	46,000	514
1,2,3,4-TeCB	4.60	4.40	2.00	9.0	6.72	1900	60
1,2,3,5-TeCB	4.59	4.39	4.18	42	6.38	5200	145
HCBD	4.90	4.70	47.1	1298	5.95	23,000	8834

[a]$f_{oc} = 0.041$
[b]From Pereira et al. (1988)
[c]From Equation 5 in text
[d]$K_{OC}^{app} = q/(C \cdot f_{oc})$
[e]From Equation 2 in text
[f]Using q, column 4, and solving Equation 4 using Excel Goal Seek
[g]DCB, TCB, TeCB, and HCBD correspond to di-, tri-, and tetra-chlorobenzene, and hexachlorbutatiene, respectively.
Field data were obtained from Pereira et al. (1988).

Table 3
Comparison of Field-Observed Sediment and Pore Water Concentrations of Phenanthrene and Benzo(a)pyrene in Tamar Estuary versus DED Isotherm Predictions

Compound and Properties			Field Measurements			Isotherm Predictions	
[a]Compound	[b]$\log K_{ow}$	[c]$\log K_{OC}^{1st}$ L/kg-OC	q mg/kg	C mg/L × 10^{+6}	[d]$\log K_{OC}^{app}$ L/kg-OC	C, [e]Linear mg/L × 10^{+6}	C, [f]DED mg/L × 10^{+6}
Phenanthrene	4.57	4.37	0.274	8.10	6.23	598	16
Benzo(a)-pyrene	6.50	6.30	0.450	5.47	6.61	33.0	8

[a]$f_{oc} = 0.020$
[b]From Schwarzenbach et al. (1992)
[c]From Equation 5 in text
[d]$q/C/f_{oc}$
[e]From Equation 2 in text
[f]DED value obtained by using q from column 4 and solving Equation 4 using Excel Goal Seek.
Field data were obtained from Readman et al. (1987).

Results and Tests of Dual-Equilibrium Desorption Model

Several scientists and engineers have made laboratory and field measurements of the three variables, q, C, and f_{OC}, needed to explicitly test the predictions of Equations 4 and 14 (Pereira et al. 1988; McGroddy and Farrington 1995). Figure 3, using 1,4-DCB, illustrates the typically excellent agreement between theory and experiment for the DED model with laboratory data. In Figure 3 the largest concentration point, about 60 mg/L, represents adsorption near the saturation limit for 1,4-DCB. All subsequent points are from stepwise desorption experiments that have been described in detail elsewhere (Chen et al. 2000c). The solid curve is drawn using the DED isotherm, Equation 4, with $f_{OC} = 0.0027$. The experiments were specially designed to eliminate the effects of slow kinetics. If desorption had proceeded along the linear isotherm, as is assumed in most models, the aqueous concentration in Figure 3 after 15 desorption steps would have been on the dashed line at ($q = 10^{-10}$ mg/kg, $C = 10^{-11}$ mg/L), well below the graph. Clearly, this did not happen. Rather, there was quantitative agreement with the predicted DED isotherm.

Data obtained at three field sites—Boston Harbor, Bayou de'Inde in Lake Charles, Louisiana, and the Tamar Estuary in England (Pereira et al. 1988; McGroddy and Farrington 1995; Readman and Mantoura 1987)—are summarized in Tables 1, 2, and 3, respectively. All of these sediments are heavily weathered and therefore expected to be characterized as being close to the second compartment section of the isotherm, Line C in Figure 1. Specific results from Tables 1, 2, and 3 for 1,4-DCB, hexachlorobutadiene, and phenanthrene are plotted in Figure 4 to compare the linear and the DED isotherms. Results for the other compounds in the tables are similar. Additional data are summarized in Figure 5.

Data on the concentrations of two PAHs and two PCBs in sediments from Boston Harbor (McGroddy and Farrington 1995) are presented in Table 1. Using the measured values of q, column 6, the

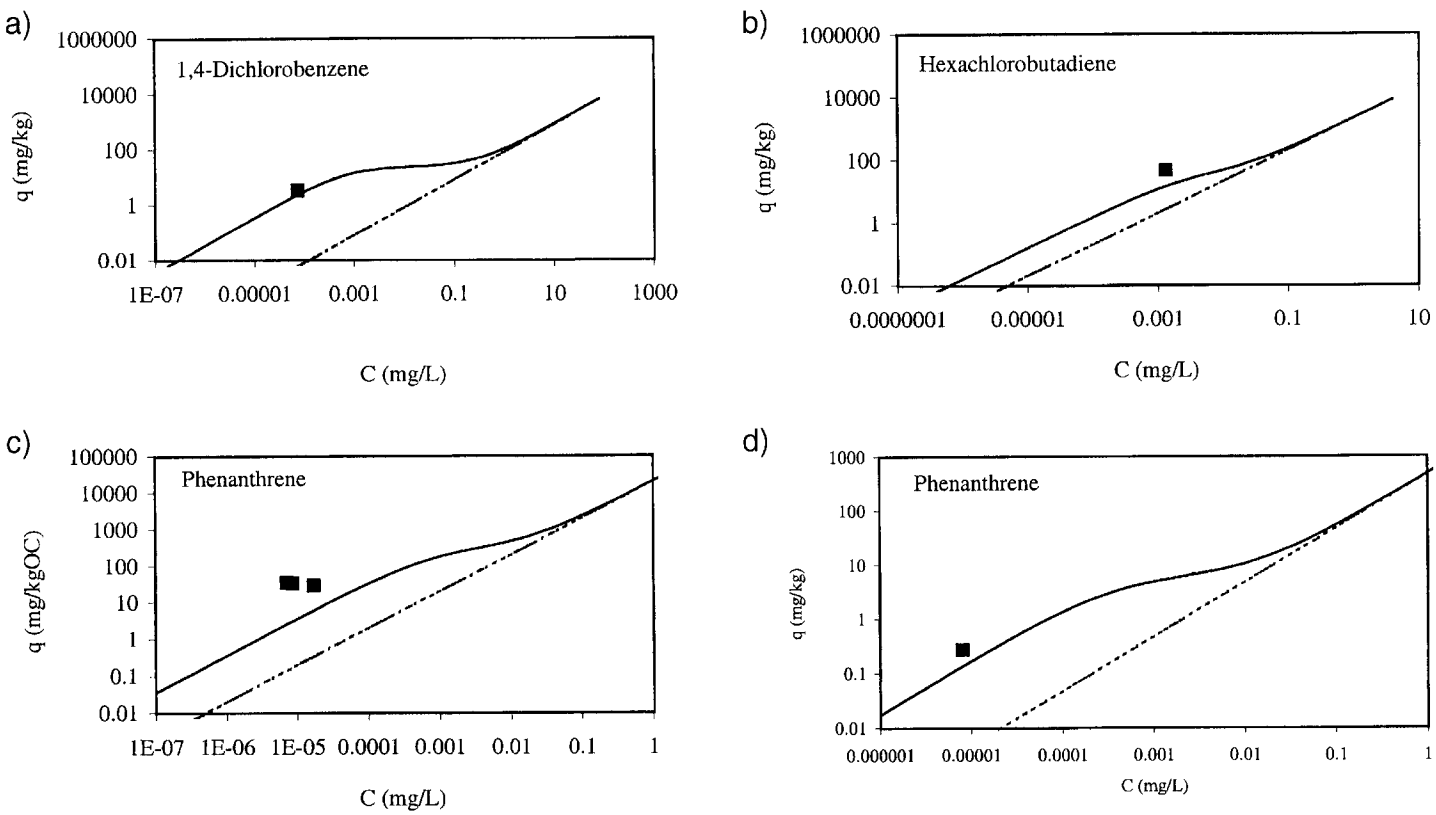

Figure 4. Plot of solid-phase concentration versus the aqueous phase concentration of model prediction and field observations. Solid curves are predicted isotherms with the dual-equilibrium desorption model (Equation 4). Dotted lines are predicted isotherms with the linear isotherm (Equation 2). Plots are: (a) field-observed sediment-pore water distributions of 1,4-dichlorobenzene in Bayou d'Inde, Louisiana, by Pereira et al. (1988); (b) field-observed sediment-pore water distributions of hexachlorobutadiene in Bayou d'Inde, Louisiana, by Pereira et al. (1988); (c) field-observed sediment-pore water phenanthrene distributions in Boston Harbor, Maine, by McGroddy et al. (1996); and (d) field-observed sediment-pore water distributions in Tamar Estuary, UK, by Readman and Mantoura (1987).

aqueous concentration, C, was predicted using the linear and the DED isotherms, columns 9 and 10, respectively. In every case, the DED isotherm-predicted value of C is as close, or closer, to the measured value as that predicted by the linear isotherm. For phenanthrene the improvement is greater than an order of magnitude. For the two PCBs, both isotherms are in reasonable agreement with the field measurements, and this is expected from the DED isotherm since the value of K_{OC}^{1st} is similar to K_{OC}^{2nd}.

Corresponding measurements of chlorinated hydrocarbons in the sediments and water of Bayou de'Inde, near Lake Charles, Louisiana (Pereira et al. 1988), are presented in Table 2; the value of $f_{OC} = 0.041$ wt/wt. For these compounds the predictive improvement of the DED isotherm over the linear isotherm is apparent in all cases, especially for the dichlorobenzenes. For example, for 1,4-DCB with a measured q = 3.36 mg/kg the linear isotherm (Equation 2) would predict C = 0.044 mg/L, whereas the DED isotherm would yield $C = 114 \times 10^{-6}$ mg/L, which is 400 times closer to the measured value of 74×10^{-6} mg/L (Table 2, column 5). For a set of PAHs, Readman and Mantoura (1987) measured the values of q, C, and f_{OC} in sediments from the Tamar Estuary in England and the results for phenanthrene and benzo(a)pyrene are summarized in Table 3. Once again, the DED isotherm matches the field data more closely than the linear model.

Also, it is important, for regulatory purposes, that the DED-predicted value of C is either essentially identical to, or larger than, the measured aqueous concentration; therefore, if the measured value of q is used to estimate C, it will probably always be an environmentally safe estimate compared to the expected measured value. Similarly, if measured values of the aqueous concentration, C, are used to estimate the amount of contaminant that could be safely left on the soil or sediment, the predicted value of q would always be equal to, or smaller than, the expected value to be measured and this would result in a safe-side estimation of the required soil remediation level. In summary, although the DED isotherm is far better than the linear isotherm to estimate actual contaminant desorption, it is still on the environmentally safe side of what is expected for both values of C and q.

Finally, comparative predictions of the linear and the DED isotherms have been tested against measurements of benzene desorption versus time for about five years at a UST site in Texas (site no. 97651; Mobil Oil Corporation 1996), Figure 6. Ground water samples were collected at regular intervals from a well that was 60 feet from the principal source. The linear and the DED isotherms were put into the respective retardation equations, Equations 12 and 14, and these were put into the one-dimensional advective transport equation, Equation 10, and solved using a Euler's Forward-Time-Central-Space finite difference approach (numerical analysis was performed using ISAST, written in Visual Basic for Application in Excel; Chen 1999). The aquifer parameters were estimated or taken from similar systems in the vicinity: (θ =

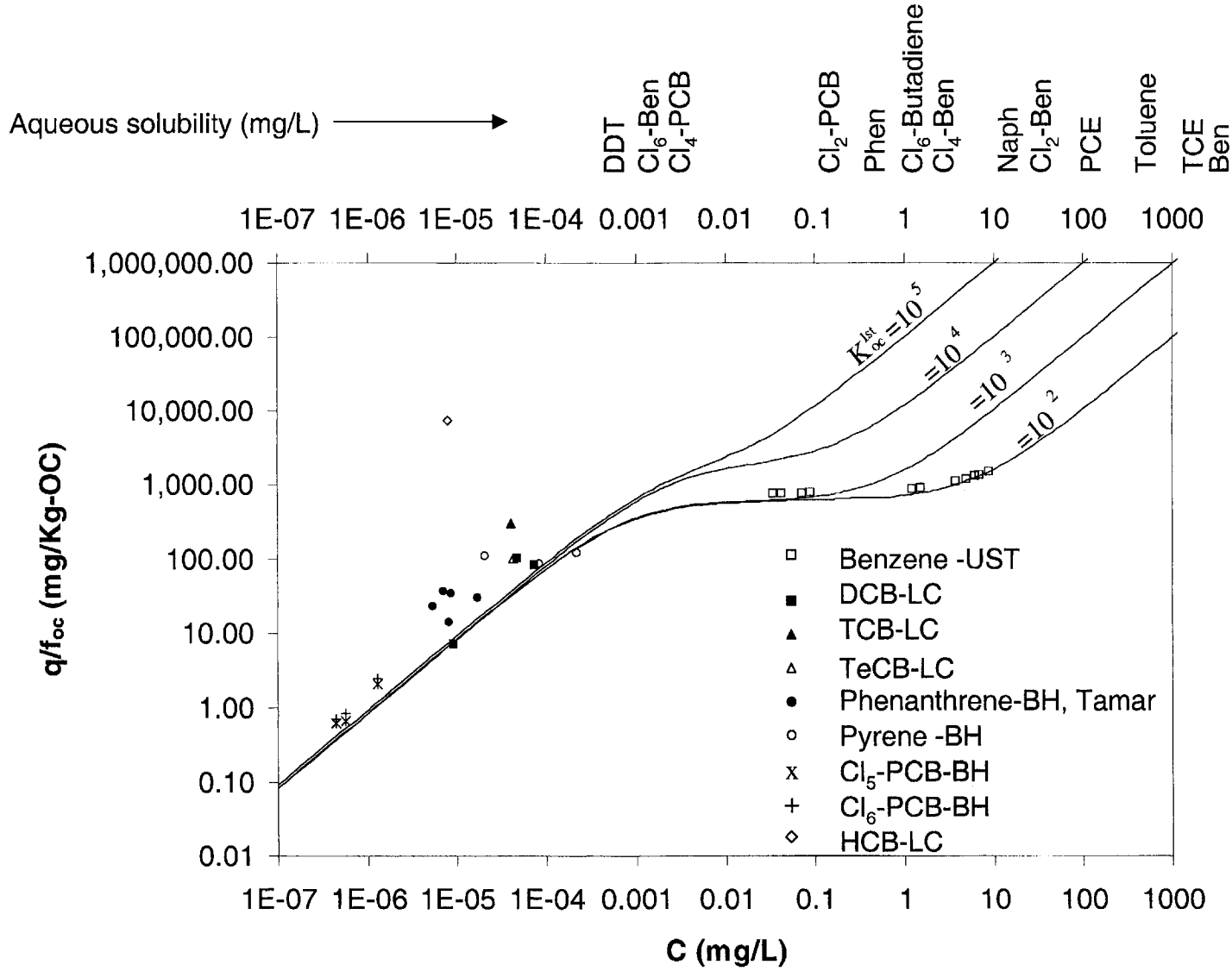

Figure 5. Plot of solid-phase concentration (mg/Kg-OC) versus the aqueous phase concentration (mg/L) of model prediction and literature reported data. The solid curves are DED desorption isotherm for compounds with log K_{OC}^{1st} values ranging from 2 to 5, log K_{OC}^{2nd} = 5.92, q_{max}^{2nd} estimated from Equation 7 of the text, and C_{sat} estimated from Equations 7–14 of Schwarzenbach et al. (1993). The symbols are literature reported data, where benzene data are from Texas UST site (no. 97651, Mobil 1996), DCB (dichlorobenzene), TCB (trichlorobenzene), TeCB (tetrachlorobenzene), and HCB (hexachlorobenzene) are from Lake Charles, Louisiana (LC, Periera et al. 1988). Phenanthrene, pyrene, and PCB data are from Boston Harbor, Maine, and Tamar Estuary (BH, McGroddy et al. 1995 and Readman and Mantoura 1987).

Table 4

Texas Natural Resource Conservation Commission (TNRCC) Tier 1 Protective Concentration Levels

Contaminant	K_{OC} [from TRRP Rule Figure 30TAC350.73(e)] (L/Kg)	Tier 1 Residential Ground Water PCL (mg/L)	Generic Dilution Attentuation Factor* (–)	Leachate Concentration Needed to Achieve GW PCLs (mg/L)	Tier 1 Residential Soil PCL in Equilibrium with Leachate (Linear Model) (mg/Kg)*
Benzene	66	0.005	20	0.1	0.026
MTBE	14.1	0.24	20	4.8	0.61
PCE	154.9	0.005	20	0.1	0.05
Vinyl chloride	11	0.002	20	0.04	0.022

*Assuming a 0.5 acre source area.
PCL: protective concentration level
TNRCC default values: fraction organic carbon, f_{OC} = 0.002; soil density, ρ_b = 1.67 g/cm^3; water-filled porosity, θ_{ws} = 0.16; air-filled porosity, θ_{as} = 0.21; dimensionless Henry's law coefficient for benzene, MTBE, PCE, and VC, H = 0.227, 0.0244, 0.765, and 3.49 (-), respectively (TNRCC 1999).

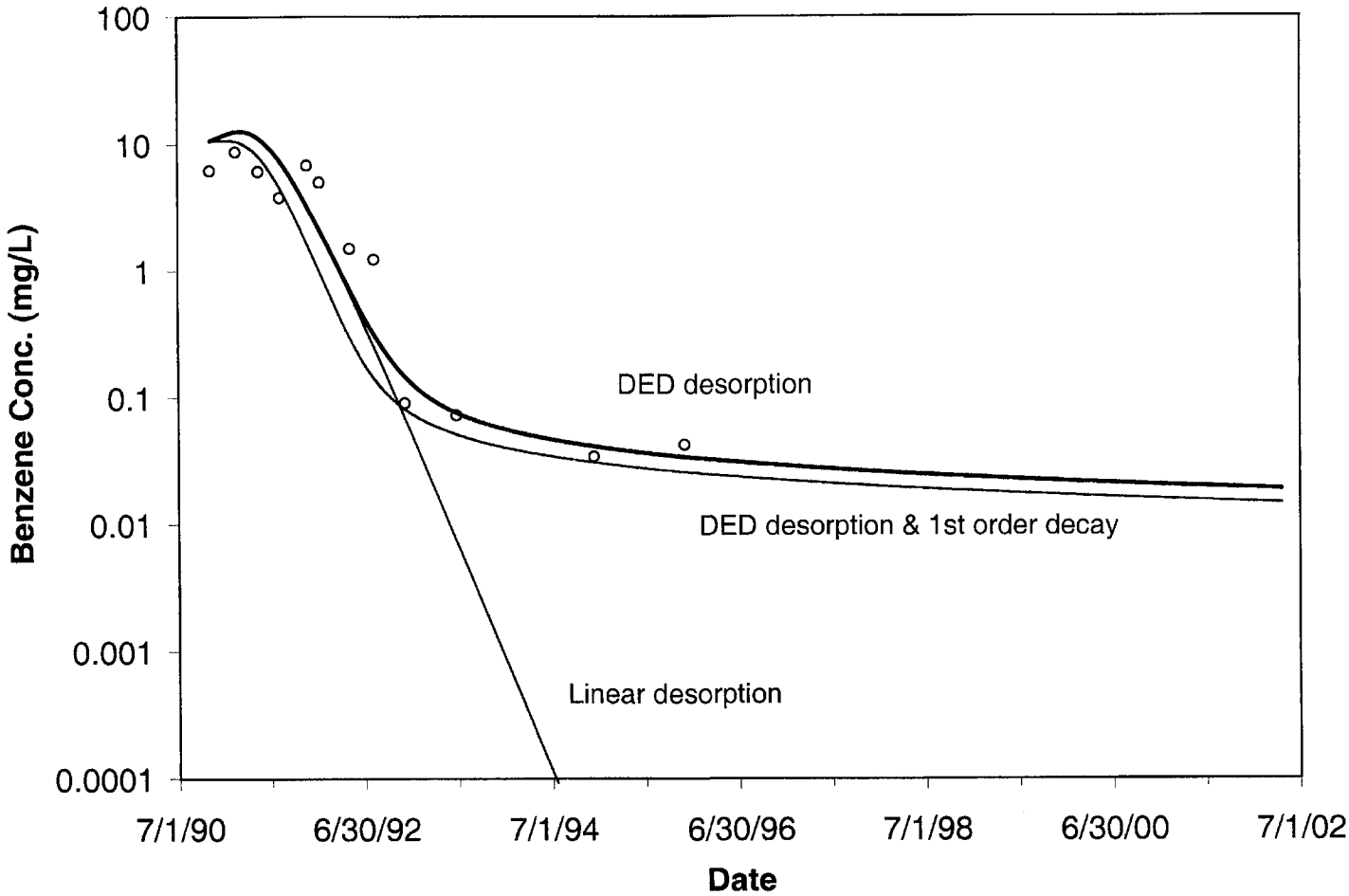

Figure 6. Plot of the ground water benzene concentration versus time from an underground storage tank (UST) site in Texas (site no. 97651). The solid curves are predicted from a linear desorption isotherm, the DED desorption isotherm, and the DED desorption isotherm coupled with a first-order decay. See text for fitting parameters.

0.3; $\rho_b = 1.67$ g/cm^3; $f_{OC} = 0.002$ wt/wt; $v = 0.3$ ft/day; and $D = 1.4$ ft^2/day (Moore 2000). The only benzene-specific parameters needed are $K_{ow} = 10^{2.13}$ or $K_{OC}^{1st} = 66$, Table 4, (TNRCC 1999), and $C_{sat} = 1800$ mg/L. The degradation rate constant, $\lambda = 0.003$ day^{-1}, was selected from experience with benzene and simply illustrates the effect of slow biodegradation in the aqueous phase on transport (Wiedemeier et al. 1999). Figure 6 shows excellent agreement with the observations for the five years over which data were available. The rapid, log-linear, decline in benzene concentration from February 14, 1991, to December 3, 1992 (658 days) is due to desorption of benzene from the first compartment. If desorption continued to follow this first desorption isotherm, remediation to the protective concentration level (PCL) value of 0.005 mg/L would have been reached in December 1993, and the concentration for the last sample point, Novembr 30, 1995 (1850 days), would have been ~ $10^{-5.5}$ mg/L (model prediction). However, after the initial rapid decrease, desorption was controlled by the second compartment and, thus, the concentration in the center of the plume leveled off to a relatively low value.

The impact of dual-equilibrium desorption (DED), as shown in Figure 6, is likely one of the factors responsible for the long-term persistence of ground water plumes. Multiple-site studies ("plume-a-thon" studies) of fuel hydrocarbon sites in California and Texas (271 sites, Rice et al. 1995; and 217 sites, Mace et al. 1997) classified the life-cycle of hydrocarbon plumes using four categories: expanding, stable, shrinking, and most significantly, exhausted. Exhausted plumes, identified by insignificant temporal changes in length and mass with average plume concentrations not greater than 1 ppb (Rice et al. 1995), comprised 47 out of 271 plumes (17%) in the California study, and 25 out of 227 plumes (11%) in the Texas study (Newell and Connor 1998). Nonetheless, neither study identified why exhausted plumes were observed and why they persisted despite the presence of vigorous bioremediation processes, which were largely able to manage the contaminant loadings from active sources (largely NAPL dissolution). At such low concentrations, it is unlikely that NAPL is still widespread at these sites, and commonly accepted conceptual models of BTEX biodegradation do not include a low-concentration threshold where BTEX biodegradation shuts down.

The presence of these exhausted plumes, however, can be readily explained with DED model. As illustrated in Figure 6, the slow desorption from the second compartment serves as a continuing, low-concentration, yet long-term source to ground water after other source materials (NAPL, desorption from the first compartment) are largely depleted. Because the contaminants sorbed within the second compartment are controlled by a much larger partition coefficient, the mass flux out of the second compartment is slow compared to the mass in the second compartment. In addition, because only desorbed contaminants are bioavailable, biodegradation has little effects on the reduction of plume concentrations (Figure 6).

Table 5
Revised Texas Natural Resource Conservation Commission Tier 1 Protective Concentration Levels If Availability Is Considered Using Dual-Equilibrium Desorption Model

Contaminant	K_{oc} [from TRRP Rule Figure 30TAC350.73(e)] (L/Kg)	Tier 1 Residential Soil PCL Using Linear Equilibrium Model (mg/Kg)*	Effective K_{oc} for Contaminant in Soil in Equilibrium with Leachate (DED Model) (L/Kg)	Revised Tier 1 Residential Soil PCL Using Model (mg/Kg)*	Times Increase in TNRCC Soil PCLs Using DED Model (–)
Benzene	66	0.026	7486	1.51	59
MTBE	14.1	0.61	55.5	1.01	1.7
PCE	154.9	0.05	5153	1.05	21
Vinyl chloride	11	0.022	9181	0.76	34

PCL: protective concentration level
DED: dual-equilibrium desorption
Porosity, density, etc., parameters are similar to those in Table 4.

Therefore, the DED model provides a plausible explanation why both multiple site studies observed exhausted plumes that appear to persist without change for relatively long time periods (years).

DED is also likely to be a factor partially responsible for the tailing effects commonly observed at pump-and-treat sites (Figure 6). The U.S. Environmental Protection Agency defines tailing as the "progressively slower rate of decline in dissolved contaminant concentration with continued operation of a pump-and-treat system" (U.S. EPA 1996). While many different isotherms are known (Ruthven 1984; Adamson 1990), most practitioners working on hydrocarbon sorption and desorption have used either a linear or a Freundlich model to represent sorption, DED is a previously unidentified tailing mechanism that is likely to be important at many pump-and-treat sites.

Impact of Dual-Equilibrium Desorption on Soil Leaching Models

Use of the linear equilibrium isotherm in soil-leaching model assumes that the entire sorbed mass of a contaminant is equally available and therefore poses the same risk to ground water from leaching. The model assumes that no nonaqueous phase contaminants are present in the soils. The relationship used to partition contaminants between leachate and unsaturated soils is shown in

$$C_L = \frac{C_T}{\left(\frac{\theta_{ws}}{\rho_b} + K_{OC} \cdot f_{OC} + \frac{H \cdot \theta_{as}}{\rho_b}\right)} \qquad (15)$$

where C_T (mg/kg) is the bulk contaminant concentration from (air + water + soil), as if all of the contaminant were on the solid soil phase; C_L (mg/L) is the concentration of contaminant in the soil leachate; H (cm^3-H_2O/cm^3-air) is the Henry's law constant for the contaminant; θ_{as} (cm^3-air/cm^3-soil) is the volumetric air content of the vadose zone soil; θ_{ws} (cm^3-H_2O/cm^3-soil) is the volumetric water content of the vadose zone soil; and the other terms are as defined in the text previously.

TNRCC uses Equation 15, protective concentration levels (PCLs) for ground water (i.e., MCLs for most contaminants), and generic dilution factors (e.g., a factor of 20 for a 0.5 acre source area) to establish Tier 1 PCLs for managing risks due to contaminated soils in Texas. These Tier 1 soil PCLs are used in site assessment and may be applied as remediation goals. In Table 4 are shown TNRCC PCL values for both ground water and soil, the associated leachate values, and the K_{OC} values used by the TNRCC for four common contaminants: benzene, methyl-tert butyl ether, perchloroethene, and vinyl chloride.

Because the partition of organic contaminants between soil and ground water is better represented by the DED model, it probably should be used to calculate effective-K_{OC} values in Equation 15. The revised soil PCL values are reported in Table 5, column 5. According to the DED model, the effective K_{OC} value used in Equation 15 for benzene at 0.10 mg/L is 7486 L/kg organic carbon, instead of 66, as in Table 4. When this effective K_{OC} is used in Equation 15, the revised soil PCL is 1.51 mg/kg, a 59-fold increase over the 0.026 mg/kg derived with the linear model. Table 5 shows similar results for the other three ground water contaminants.

If these revised PCL values based on the present DED model (Table 5, column 5) were used, many of the soil remediation projects that are now conducted for the purpose of protecting ground water would not be required. Benzene leaching from soil drives most of the soil remediation projects at UST sites. Thus, incorporation of the DED model indicates that many soils at UST sites are not sufficiently contaminated to cause an exceedence of the drinking water standard for benzene (0.005 mg/L) through soil leaching.

Additionally, the retardation factor, R, increases as the concentration decreases, as can be illustrated using benzene with $f_{OC} = 0.002$ in Equation 14. Values of R for benzene change dramatically over the range of concentrations of interest to remediation, as illustrated for the following data pairs (C mg/L, R): 10^{-4} mg/L, 7510; 10^{-3} mg/L, 2080; 5×10^{-3} mg/L, 218; 10^{-2} mg/L, 65; and 1 mg/L, 1.7. The increase in retardation factors associated with a decrease in ground water concentrations greatly limits the efficiency of flushing systems, either pump and treat or natural flushing from ground water flow. At the same time, the environmental risk is predicted to be greatly reduced over what had been previously expected using linear desorption models.

Summary and Conclusions

A new dual-equilibrium desorption (DED) model has been developed and illustrated using a wide range of laboratory and field data; the consequences of this new model to sediment contamination and ground water remediation have been illustrated using a range of compounds and conditions. Compared to the commonly adopted desorption models, the DED model can more accurately quantify the release of the organic contaminants from soil and sediments, especially at low concentrations. The DED model

requires only simple parameters, including K_{ow}, solubility and f_{OC}; all can be easily obtained. The DED isotherm can be readily incorporated into standard models of transport and risk.

A typical DED curve illustrates how desorption will likely progress for a specific contaminant-soil combination. Thus, when constructed, a DED curve such as those in Figures 1 and 3 can be used to understand q-C relationship under various environmental conditions. If neither C, q, nor f_{OC} have been measured, a reasonable f_{OC} can be assumed to construct the DED curve, which will suggest critical values of C and q for which to test and monitor. In the other extreme, if C, q, and f_{OC} have all been measured on the same or closely related samples, then an isotherm can be constructed to interpret the expected future course of desorption analogous to the discussions of Figure 1. Often, only a value(s) of C is measured in a sample well, etc.; in this case, it is recommended to assume a value for f_{OC} and construct a DED isotherm and determine the value of q, which corresponds to the measured value of C. The location of the (C,q) point on the isotherm can provide an estimate of how future desorption will proceed. Similarly, other combinations of available data can be used to estimate future contaminant desorption.

In conclusion, availability of adsorbed contaminant, which can be easily accounted for using the DED model, is significant to soil-sediment leaching calculations, risk assessment, and ground water remediation projects. Accounting for DED effects indicates that many sites with contaminated soils that do not contain NAPL do not pose a risk to ground water and may not require remediation. When DED effects are accounted for in ground water flushing, the amount of flushing required may dramatically increase for most common ground water contaminants. The DED model provides one explanation why pump and treat systems appear to be an inefficient remediation approach, and can help explain the observation of "exhausted" plumes where low concentrations persist for long time periods.

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