ground water

Computer Note/

A Program for Evaluating Dual-Equilibrium Desorption Effects on Remediation

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Abstract

Desorption is one of the most critical processes affecting the effectiveness of soil and ground water remediation. None of the currently adopted desorption models can accurately quantify desorption of low-hydrophobicity organic chemicals, and thus could potentially mislead remediation design and decision-making. A recently developed dual-equilibrium desorption (DED) model was found to be much more accurate in quantifying desorption. A screening-level transport model, DED-Transport, was developed to simulate the DED effect on behaviors of organic contaminant plumes during remediation. DED-Transport requires only simple parameters, but is applicable to many remediation scenarios. DED-Transport can be used as a decision-support tool in site remediation to more precisely predict the time required for cleanup.

Introduction

Contaminant desorption is one of the most important processes affecting site remediation, but often receives little attention in remedial design. Desorption of contaminants from soils or sediments often cannot be modeled accurately with the conventional desorption models. All the currently adopted desorption models greatly simplify desorption by assuming that desorption is the simple reverse of adsorption and that the partition coefficients determined through sorption experiments are also applicable to desorption. However, numerous studies have shown that desorption is indeed biphasic (Figure 1)—at high concentrations, desorption is rapid, but at low concentrations, desorption is very difficult and contaminants in this region persist much longer than would be expected from conventional physical-chemical and microbial parameters (Linz and Nakles 1997). Such biphasic desorption may greatly reduce the availability of contaminants in the subsurface and, therefore, may significantly hinder soil and ground water remediation, assuming that the current cleanup standards have to be met. Thus, using the conventional desorption models in remediation design, one could greatly underestimate the costs and time associated with site remediation.

A new contaminant desorption model, called a dual-equilibrium desorption (DED) model, has been developed at Rice University based on several years of research (Chen et al. 2002). The DED model is presently the only model

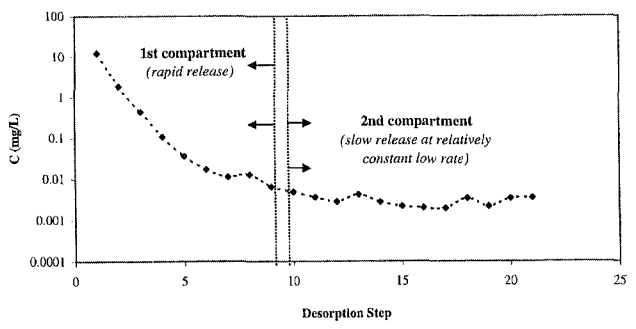

Figure 1. Plot of aqueous phase concentration vs. desorption step (Kan et al. 1997). Repetitive desorption was conducted using naphthalene and Lula soil (0.27% organic carbon). Extended desorption time was applied to the last two desorption steps—19 days and 29 days, respectively.

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available that can describe the commonly observed resistant nature of contaminant desorption from soils and sediments using known parameters. The DED model has been tested with numerous laboratory and field observations on a diverse range of organic compounds, soils/sediments, and conditions, and has been found to be much more accurate than any conventional desorption model. Once incorporated into transport equations, the DED model should considerably improve the accuracy of fate and transport study and, therefore, the efficiency of site remediation design.

In this paper, an Excel/Visual Basic screening-level contaminant transport model, DED-Transport, is presented. The program was designed to evaluate the DED effect on site remediation by incorporating the DED model in standard transport equations. DED-Transport is intended to serve as a decision-support tool for remediation design.

Numerical Approach

A DED model has been developed to quantitatively describe the commonly observed biphasic desorption phenomenon. In the DED model, sorption is assumed to be a linear combination of the first and second compartments. The general DED isotherm model can be expressed as (Chen et al. 2002)

$$q = K_{OC}^{1st} \times f_{OC} \times C + \frac{K_{OC}^{2nd} \times f_{OC} \times q_{\max}^{2nd} \times C}{q_{\max}^{2nd} + K_{OC}^{2nd} \times f_{OC} \times C} \quad (1)$$

An important aspect that is not presently available for any other biphasic desorption theory is that all of the necessary chemical parameters in Equation 1 can be readily obtained. The value of K_{OC}^{1st} (L/kg organic carbon) can be obtained from numerous tabulations, specific correlations, and explicit measurement. The value of K_{OC}^{2nd} (L/kg organic carbon) has been found to be a single constant for all hydrophobic compounds tested to date, for at least 41 data sets (Chen et al. 2002):

$$\log K_{OC}^{2nd} = 5.92 \pm 0.16 \quad (2)$$

$q_{\max}^{2nd}$ (mg/kg) can be calculated with the following equation:

$$q_{\max}^{2nd} = f_{OC}(K_{OW}C_{sat})^{0.534} \quad (3)$$

where K_{OW} (L water/L octanol) is the octanol-water partition coefficient; and C_{sat} (mg/L) is the aqueous solubility (Chen et al. 2002). Note that the biphasic effect is more significant for organic chemicals with low hydrophobicity (e.g., benzene and dichloroethene) because the difference between K_{OC}^{1st} and K_{OC}^{2nd} is more profound for such compounds (Figure 2). For a more detailed discussion of how to calculate K_{OC}^{1st} and of why a single constant K_{OC}^{2nd} value can be used for any chemical/soil combination, see Kan et al. (1998), Chen et al. (2000), and Chen et al. (2002).

Since the DED model is much more accurate in quantifying desorption, it should probably be used in transport equations to replace the conventional desorption terms, so

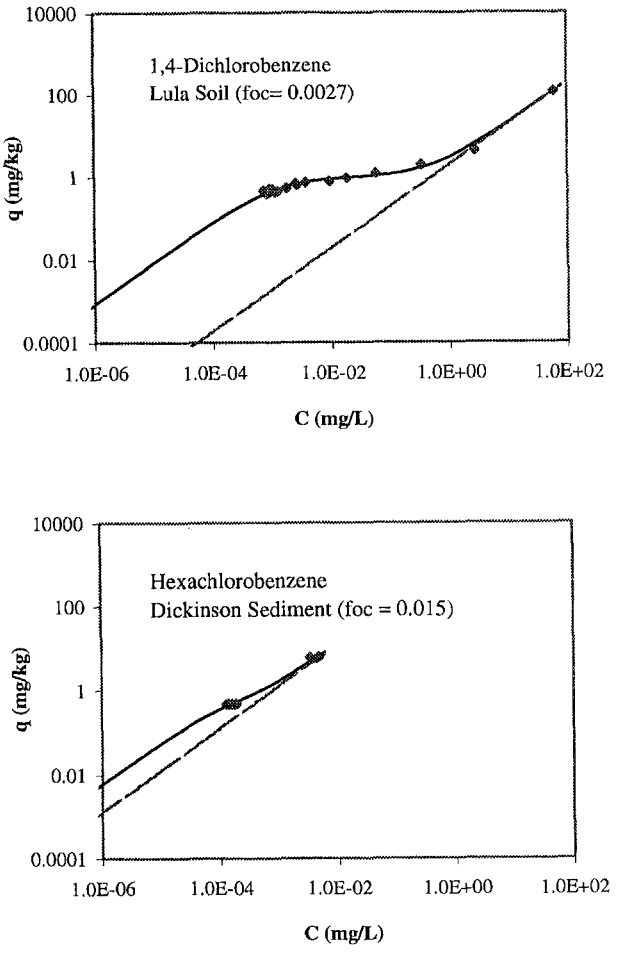


Figure 2. Plot of solid phase concentration vs. aqueous phase concentration of model predictions and laboratory observations. Solid curve is the expected DED curve and the dashed line is the expected linear desorption curve. The data points are experimental desorption results (Chen et al. 2000).

that the fate and transport of contaminants in the subsurface can be more accurately modeled. This is particularly important toward the later stage of site remediation, when soils are well washed (flushed) and the adsorbed contaminants are predominantly associated with the second compartment. At this stage, desorption is very difficult and the extent of desorption predicted using the conventional models can be orders of magnitude higher than what would happen in reality.

The governing equation for the one-dimensional transport of a solute in ground water is given by

$$\frac{\partial C}{\partial t} + \frac{\rho}{n}\frac{\partial q}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - \lambda C \quad (4)$$

where C is the solution-phase concentration (M/L^3) of a chemical; q is the solid phase concentration (M/M); D is the hydrodynamic dispersion coefficient (L^2/T); v is the seepage velocity (L/T); ρ is the soil bulk density (M/L^3); n is the effective porosity (dimensionless); λ is the first-order decay coefficient (T^{-1}); x is the distance (L); and t is the time (T).

When using the DED model to describe desorption, the correlation between the solid and aqueous phase concentrations is described with Equation 1. Differentiating the solid phase concentration q with regard to time yields

$$\frac{\partial q}{\partial t} = \left(K_{OC}^{1st} f_{OC} + \frac{K_{OC}^{2nd} f_{OC} (q_{max}^{2nd})^2}{(q_{max}^{2nd} + K_{OC}^{2nd} f_{OC} C)^2} \right) \frac{\partial C}{\partial t} \quad (5)$$

When Equation 5 is plugged into Equation 4, the governing equation becomes

$$\left[1 + \frac{\rho}{n} \left(K_{OC}^{1st} f_{OC} + \frac{K_{OC}^{2nd} f_{OC} (q_{max}^{2nd})^2}{(q_{max}^{2nd} + K_{OC}^{2nd} f_{OC} C)^2} \right) \right] \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \lambda C \quad (6)$$

Equation 6 can be solved numerically. The simplest numerical integration method is probably the Eulerian finite-difference method, which can be used with any spatial or temporal interpolation scheme (Remson et al. 1970). For example, Euler's Forward-Time Center-Space (FTCS) approach can be used to solve the governing transport equations; i.e., the differentiation of concentration with time at a certain location is approximated by a forward differencing scheme.

Description of Computer Program

A screening-level solute transport model—DED-Transport—was developed by solving Equation 6 with Euler's FTCS approach. The software is programmed in Excel/Visual Basic (available through the authors upon request). The program has the ability to simulate the effects of advection, dispersion, desorption, and degradation/mass removal on plume behaviors at contaminated sites. DED-Transport was not designed to simulate the migration of plumes from the source areas; such models are widely available (e.g., BIOSCREEN and MT3D). Rather, DED-Transport is intended to be used to evaluate the plume behavior during remediation and in the postremediation period, especially to evaluate the effects of biphasic desorption on remediation as opposed to the linear desorption that is most commonly assumed in remediation design. This is an important aspect that cannot be addressed with any transport model currently available.

Although DED-Transport is a simple model, it can provide quantitative results for a number of remediation scenarios, such as:

1. Postremediation concentration changes in monitor wells in natural conditions.
2. Effect of pump and treat, simulated by increasing ground water seepage velocity.
3. Effect of enhanced bioremediation, simulated by assigning a site-specific decay constant.
4. Effects of other mass removal mechanisms (e.g., air-sparging), simulated by assigning a lumped decay constant.

DED-Transport can also provide semiquantitative results for some other remediation scenarios. For example, during in situ oxidation (e.g., using permaganate), soil organic matters are destroyed by oxidation reactions, causing more contaminants being released. This effect can be simulated by assigning a smaller f_{OC} value to the model.

The conceptual model of DED-Transport can be illustrated using Figure 3. The plume is represented with the darker areas in the figure, with higher concentration near the source. When upgradient ground water flows through the affected area, contaminants are removed gradually and the concentrations decrease. The model output is designed to show the changes of concentrations along the center flow line with time in various conditions.

The model input window of the program is illustrated in Figure 4. The following parameters are generally required for model input. The hydrogeological parameters include soil bulk density, ρ (kg/L); aquifer effective porosity, n (dimensionless); fractional organic carbon, f_{OC} (dimensionless); and ground water seepage velocity, v (ft/day). The chemical-biochemical parameters include dispersion coefficient, D (ft^2/day); octanol-water partition coefficient, K_{OW} (L/kg); aqueous solubility, C_{sat} (mg/L); organic carbon normalized partition coefficient, K_{OC} (L/kg); and first-order decay coefficient, λ (day^{-1}). Finally, the modeling parameters include inflow concentration, C_0 (mg/L) (typically $C_0 = 0$); spatial dimension, X (ft); and simulation time, T (day).

Note that D can be input either directly or by specifying an estimated plume length (Xu and Eckstein 1995):

$$D = v \times 3.28 \times 0.83 \left[\mathrm{Log}_{10} \left(\frac{L_p}{3.28} \right) \right]^{2.414} \quad (7)$$

where L_p (ft) is plume length. Similarly, a user has the option of inputting the half-life of the solute, $t_{1/2}$ (day), instead of λ. Other parameters, including K_{OC}^{2nd}, q_{max}^{2nd}, Δx, and Δt, are typically generated by the model. However, a user can also overwrite the default values by manually inputting desired values. An example is illustrated in Figure 4, using benzene as the constituent of concern and assuming typical hydrogeology; the values of K_{OW}, C_{sat}, and K_{OC}^{1st} for benzene are from Knox et al. (1993) and K_{OC}^{2nd} is the default value, $10^{5.92}$, as recommended for all the chemical-soil combinations.

As a screening-level model, DED-Transport assumes simplified initial and boundary conditions. For initial

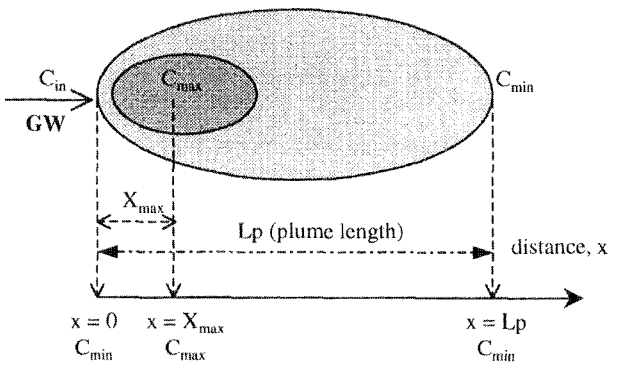
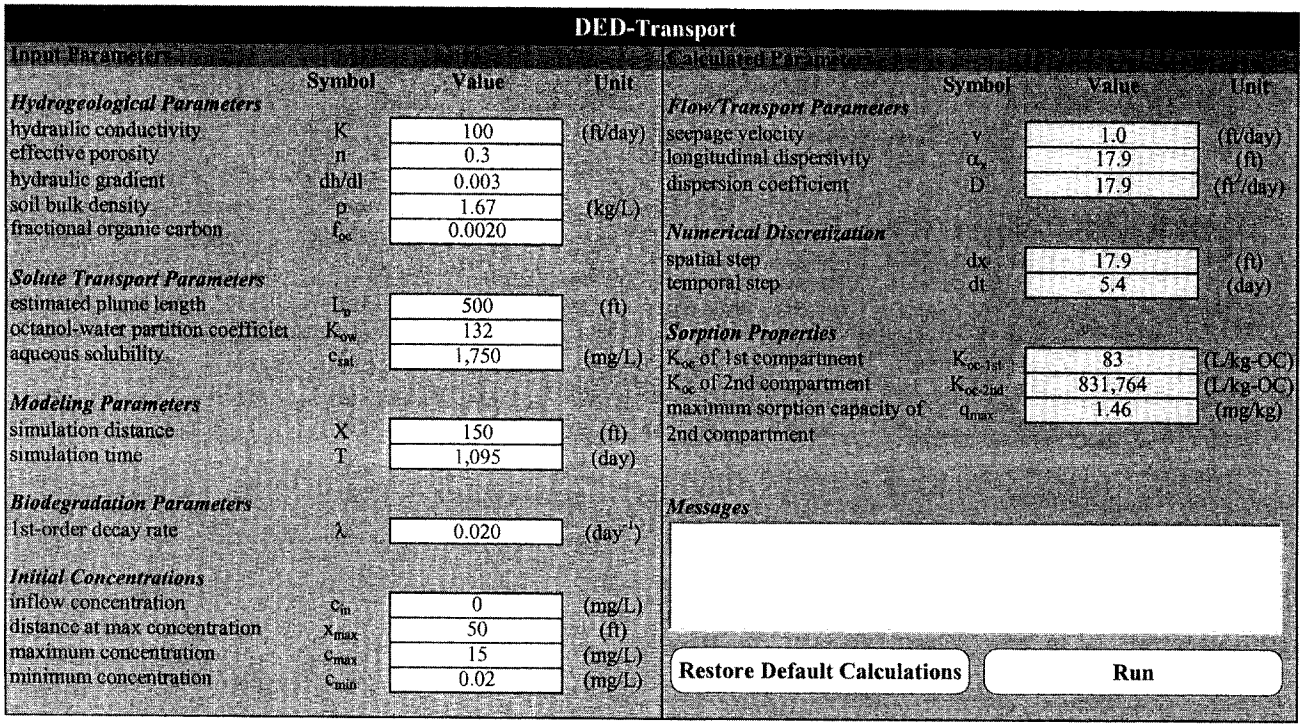


Figure 3. Illustration of the conceptual model of DED-Transport. A plume is defined by the maximum concentration, C_{max}, as well as the minimum concentration, C_{min}. Concentration at any location x along the flow pass is calculated from C_{max} and C_{min}, assuming concentrations within the plume follow logarithmic distribution.



DED-Transport

Input Parameters

	Symbol	Value	Unit
Hydrogeological Parameters			
hydraulic conductivity	K	100	(ft/day)
effective porosity	n	0.3	
hydraulic gradient	dh/dl	0.003	
soil bulk density	ρ	1.67	(kg/L)
fractional organic carbon	f_{oc}	0.0020	
Solute Transport Parameters			
estimated plume length	L_p	500	(ft)
octanol-water partition coefficient	K_{ow}	132	
aqueous solubility	c_{sat}	1,750	(mg/L)
Modeling Parameters			
simulation distance	X	150	(ft)
simulation time	T	1,095	(day)
Biodegradation Parameters			
1st-order decay rate	λ	0.020	(day^{-1})
Initial Concentrations			
inflow concentration	c_{in}	0	(mg/L)
distance at max concentration	x_{max}	50	(ft)
maximum concentration	c_{max}	15	(mg/L)
minimum concentration	c_{min}	0.02	(mg/L)

Calculated Parameters

	Symbol	Value	Unit
Flow/Transport Parameters			
seepage velocity	v	1.0	(ft/day)
longitudinal dispersivity	α_x	17.9	(ft)
dispersion coefficient	D	17.9	(ft^2/day)
Numerical Discretization			
spatial step	dx	17.9	(ft)
temporal step	dt	5.4	(day)
Sorption Properties			
K_{oc} of 1st compartment	$K_{oc\text{-}1st}$	83	(L/kg-OC)
K_{oc} of 2nd compartment	$K_{oc\text{-}2nd}$	831,764	(L/kg-OC)
maximum sorption capacity of 2nd compartment	q_{max}	1.46	(mg/kg)

Messages

Restore Default Calculations | Run

Figure 4. DED-Transport model input window. The left half of the window lists the site-specific and chemical-specific parameters. The right half lists modeling parameters typically generated by the software, but can be overwritten by a user.

concentrations, the model takes the concentration at the hottest spot (the highest concentration, C_{max}, Figure 3) and the concentration at the edge of the plume (the lowest concentration, C_{min}, Figure 3) as the input parameters. It then generates the initial concentrations in each node along the flowpath (i.e., $C_0^0, C_1^0, C_2^0, \ldots, C_m^0$) assuming that concentration follows logarithmic distribution within the plume. The model assumes that the boundary condition (concentration in upgradient ground water, i.e., $C_0^0, C_0^1, C_0^2, \ldots,$) is constant, equal to zero or a constant value. The rationale for the simplified initial conditions is that normally only the concentrations at the center and at the edge of the plume are of the highest interests. However, the model can be modified so that a user can manually specify more complex initial concentration profiles.

Application

The model output includes two graphs—the breakthrough curves, i.e., the concentration vs. time at location X (Figure 5), and the concentration profile along the flowpath (Figure 6). For example, Figure 5 includes two breakthrough curves observed at distance X assuming transport is controlled by (1) advection, dispersion, linear desorption, and first-order decay; and (2) advection, dispersion, DED, and first-order decay. Similarly, Figure 6 shows the concentration along the flowpath assuming the transport is controlled by the previous two mechanisms, respectively. In addition, the concentration vs. time data at any location can be viewed in the two worksheets of the model.

The effect of DED on soil and ground water remediation can be understood with DED-Transport. An example is shown in Figures 4 through 6 to illustrate the behavior of a benzene plume during remediation, assuming commonly observed site conditions in Texas. In Figure 5, the concentration within the plume decreases rapidly if solute transport is controlled by advection, dispersion, and linear desorption. However, if transport is controlled by advection, dispersion, and DED, the concentration remains relatively constant after an initial rapid decrease. This indicates that the DED effect could greatly extend the time required to clean up a contaminated site to the current regulatory standards, such as maximum contaminant levels. Similarly, Figure 6 shows that if desorption is controlled by DED, the concentration of contaminants can persist at much higher concentrations than would be expected assuming linear desorption, even after extensive treatment. The DED effect

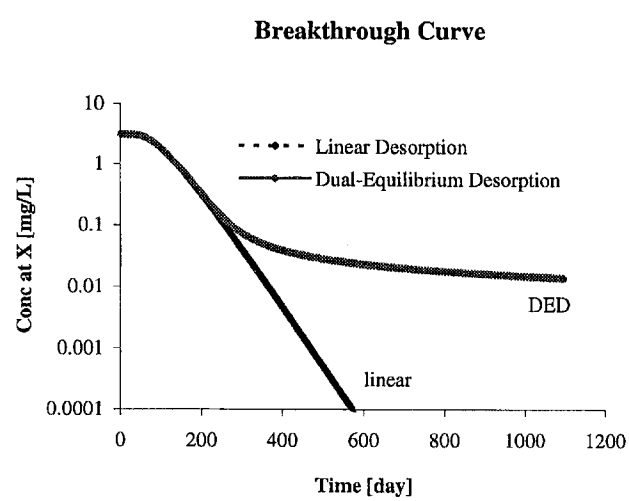


Figure 5. DED-Transport output graph—breakthrough curves at the simulation distance X. The two curves represent transport controlled by (1) advection, dispersion, linear desorption, and first-order decay; and (2) advection, dispersion, DED, and first-order decay.

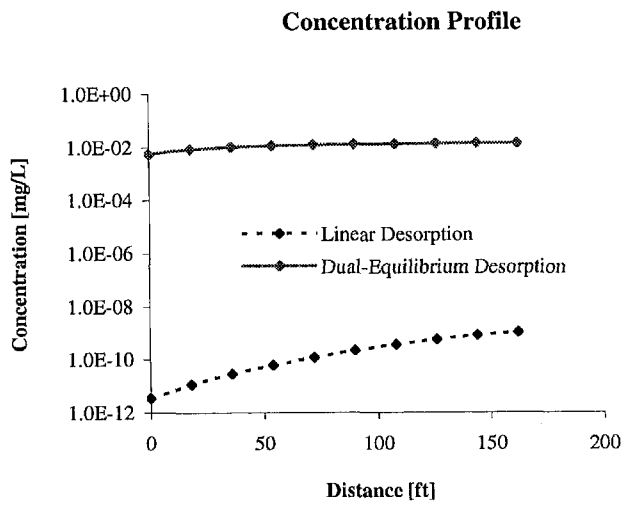


Figure 6. DED-Transport output graph—concentration profiles along the ground water flowpath in a plume at the simulation time T. The two curves represent transport controlled by (1) advection, dispersion, linear desorption, and first-order decay; and (2) advection, dispersion, DED, and first-order decay.

is especially significant for chemicals that are relatively less hydrophobic, such as benzene and chlorinated solvents.

The DED effect is likely an important factor responsible for the long-term persistence of ground water plumes. Studies of multiple fuel hydrocarbon sites have shown that after an initial rapid decline, the plume concentration remains constant for years (Newell and Connor 1998). This scenario is contradictory to the common fate and transport theories, because at such low concentrations it is unlikely that nonaqueous phase liquid is still widespread at these sites, and commonly accepted benzene, toluene, ethylbenzene, and xylene (BTEX) biodegradation mechanisms do not include a low-concentration threshold where BTEX biodegradation shuts down. Such a scenario, however, is consistent with the DED-Transport model presented here (Figure 5). Moreover, while remediation processes such as bioremediation and air-sparging may greatly facilitate mass removal from ground water, these processes have little effect on the overall mass removal because at this stage of remediation, desorption is the rate-limiting factor. Therefore, the DED effect is a plausible reason why plumes appear to persist for relatively long periods of time. Similarly, DED is likely a previously unidentified factor causing the commonly observed rebound effect at contaminated sites after the completion of remedial activities.

Conclusion

The DED effect on soil and ground water remediation is paradoxical. On one hand, the DED effect seems to result in much longer remediation processes. On the other hand, the same effect often causes soil/ground water contaminations to be lesser problems than what would normally be expected (Figure 2). For the site conditions described in Figure 2, assuming the measured soil concentration of 1,4-dichlorobenzene is 0.5 mg/kg, the ground water concentration estimated using the conventional approach (e.g., the linear model) would be ~0.25 mg/L, but in reality, the ground water concentration is more likely to be 0.0012 mg/L (due to the DED effect), which is more than 200 times lower. Put another way, because the DED effect makes desorption very difficult, it may greatly reduce the risks of contaminated soils through leaching to ground water. Thus, many affected sites may not even require active soil and ground water remediation (Chen et al. 2002).

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