

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 hydrocarbon 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 BTEX and PAHs. 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 (UST) 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 and groundwater contamination often drives site remediation. According to USEPA (U. S. Environmental Protection Agency, 1987), 217,000 sites with identified soil or groundwater problems required remediation, while new sites continue to emerge nationwide. Subsurface remediation can be very expensive yet ineffective, in that the average remediation time ranges from 10 to 30 years and the average cost per site approaches \$ 1 million, not including the cost of post-remediation monitoring (U. S. Environmental Protection Agency, 1987). Many innovative site remediation technologies (e.g., soil vapor extraction/air sparging, surfactant flushing, enhanced bioremediation, in-situ oxidation, thermal desorption, etc.) have been developed over the last decade. While these new approaches may be more cost-effective than the traditional approach comprising mainly excavation and pump and treat, their performance has not always been encouraging. Soil and groundwater remediation technologies fail to work for two main reasons: 1) complex site geology and hydrogeology (which cause difficulties in source characterization and in delivery of remediation reagents); and 2) lack of understanding of physical, chemical and microbial processes controlling remediation.

Contaminant desorption is one of the most important processes affecting site remediation but often receives little attention in remedial design. Nonetheless, it is well accepted that only desorbed contaminants are available to remediation, either chemically or biologically. Thus, precisely evaluating the extent of desorption is critical in remediation design. In reality, 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 bi-phasic (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, D.G. & Nakles, D.V., 1997). Such bi-phasic desorption may greatly reduce the availability of contaminants in subsurface and therefore may significantly hinder soil and groundwater 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 “dual-equilibrium desorption” (DED) model, has been developed at Rice University based on several years of research (Chen, W., et al, 2002). The DED model is presently the only model 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, the background and theory behind the DED model is briefly introduced. The impact of DED on fate and transport and the application of DED model in common transport equations are discussed. An Excel/Visual Basic screening-level contaminant transport model, designed to evaluate the DED effect on site remediation, is presented. This model is intended to serve as a decision-support tool for remediation design.

Background and Theory

Many laboratory and field studies have been conducted to understand the sorption and desorption of organic chemicals. A common observation is 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 (Wu, S.-C. & Gschwend, P.M., 1986; Brusseau, M.L. & Rao, P.S.C., 1989; Ball, W.P. & Roberts, P.V., 1991; Weber, W.J., Jr., McGinley, P.M. & Katz, L.E., 1992; Carroll, K.M., et al, 1994; Burgos, W.D., Novak, J.T. & Berry, D.F., 1996; Pignatello, J.J. & Xing, B., 1996; Chiou, C.T. & Kile, D.E., 1998; Kan, A.T., et al, 1998). Typically, desorption becomes very difficult after a period of weathering, in that aqueous contaminant concentrations are often much lower than what would be predicted using common sorption-desorption models. It appears that sorption and desorption are both bi-phasic, consisting of two compartments, each with unique equilibrium and kinetic characteristics (Carroll, K.M., et al, 1994; Pignatello, J.J. & Xing, B., 1996; Weber, W.J., Jr. & Huang, W., 1996). The mechanism(s) causing the bi-phasic sorption and desorption has not yet been identified; however most researchers consider the two compartments as different types of soil organic matrices, e.g., amorphous (flexible, expanded) organic carbon versus glassy (rigid, condensed) organic carbon (Pignatello, J.J. & Xing, B., 1996; Weber, W.J., Jr. & Huang, W., 1996), soil organic matter versus high-affinity (Chiou, C.T. & Kile, D.E., 1998), and adsorption to sediment surface versus entrapment in sediment pores (Adamson, A.W., 1990; Farrell, J. & Reinhard, M., 1994).

A dual-equilibrium desorption (DED) model has been developed to quantitatively describe this bi-phasic desorption phenomenon. In the DED model, sorption is assumed to be a linear combination of the first and second compartments:

$$q = q^{1st} + q^{2nd} \quad (1)$$

where q (mg/kg-soil) represents total sorption; and q^{1st} and q^{2nd} (mg/kg-soil) represent sorption to the 1st and 2nd compartments. Sorption to the 1st compartment follows the linear isotherm while sorption to the 2nd compartment can be described with a Langmuir-type isotherm (Kan, A.T., et al, 1998):

$$q^{1st} = K_{OC}^{1st} \cdot f_{OC} \cdot C \quad (2)$$

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

where: C (mg/L) is the aqueous concentration of the contaminant; K_{OC}^{1st} and K_{OC}^{2nd} (L/kg-OC) are the organic carbon normalized partition coefficients for the 1st and 2nd compartments, respectively; q_{max}^{2nd} is the maximum sorption capacity of the 2nd compartment (mg/kg-soil); f_{OC} is the fractional organic carbon; and f is the fraction of the 2nd compartment that is saturated upon exposure. It has been shown for field systems that assigning a value of f equal to one is reasonable (Kan, A.T., et al, 1998) and will always yield a conservative estimate of q . Combining Equations 1, 2, and 3 and assuming $f = 1$, the general DED isotherm model can be expressed as (Kan, A.T., et al, 1998)

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

An important aspect that is not presently available for any other bi-phasic desorption theory is that all of the necessary parameters in Equation 4 can be readily obtained. The value of K_{OC}^{1st} can be obtained from numerous tabulations, specific correlations and explicit measurement. The value of K_{OC}^{2nd} has been found to be a single constant for all hydrophobic compounds tested, to date:

$$\log K_{OC}^{2nd} = 5.92 \pm 0.16, \quad n = 41 \quad (5)$$

q_{max}^{2nd} can be calculated with the following equation:

$$q_{\max}^{2\text{nd}} = f_{\text{OC}} (K_{\text{OW}} C_{\text{sat}})^{0.534} \quad (6)$$

where K_{OW} (L-water/L-octanol) is the octanol-water partition coefficient; and C_{sat} (mg/L) is the aqueous solubility (Chen, W., et al, 2002).

Note that the bi-phasic effect is more significant for organic chemicals with low hydrophobicity (e.g., benzene and dichloroethene) because the difference between $K_{\text{OC}}^{1\text{st}}$ and $K_{\text{OC}}^{2\text{nd}}$ is more profound for such compounds. For highly hydrophobic chemicals (e.g., hexachlorobenzene and DDT), since $K_{\text{OC}}^{1\text{st}}$ and $K_{\text{OC}}^{2\text{nd}}$ are very close, the DED model and the conventional linear model are very similar (refer to Figure 2).

While Equations 1 and 4 are probably the most widely applicable, there are situations wherein Equations 1 and 4 need to be modified to quantify the presence of other specific processes, such as free phase contaminant, colloid, surfactant, co-solvent, total petroleum hydrocarbon (TPH), and other types of non-aqueous phase liquids (NAPL). These are discussed in detail in Chen et al. (Chen, W., et al, 2002).

The DED model is based on extensive laboratory experiments using a number of chemicals and many different soils and sediments (Kan, A.T., Fu, G. & Tomson, M.B., 1994; Kan, A.T., et al, 1998; Chen, W., Kan, A.T. & Tomson, M.B., 2000). It has been tested using a wide range of laboratory and field data from other scientists ((Readman, J.W. & Mantoura, R.F.C., 1987; Pereira, W.E., et al, 1988; McGroddy, S.E. & Farrington, J.W., 1995). The model has also been used to explain key observations related to underground storage tank sites (Chen, W., et al, 2002). Overall, it has been found that the DED model is much more accurate than conventional desorption models. Detailed comparisons between the DED model predictions and field observations are included in Chen et al. (Chen, W., et al, 2002).

Recently, a new single step laboratory extraction procedure using cosolvents has been developed to independently measure the amount of contaminant in the second, resistant, compartment. Results using this new procedure, are in quantitative agreement with these equations. Detailed results of these studies will be published elsewhere.

Application of DED in Transport Modeling

Since DED model is much more accurate in quantifying desorption, it should probably be used in transport equations to replace the conventional desorption terms, so that the fate and transport of contaminants in subsurface can be more accurately modeled. This is particularly important toward the later stage of site remediation, when soils are well weathered and the adsorbed contaminants are predominantly associated with the 2nd 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 advective-dispersive transport of a solute in groundwater is given by:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (7)$$

where C is the solution-phase concentration (M/L^3) of a chemical; D is the hydrodynamic dispersion coefficient (L^2/T); v is the seepage velocity (L/T); x is the distance (L); and t is the time (T). When sorption/desorption and first order decay are considered, the governing equation can be modified as:

$$\frac{\partial C}{\partial t} + \frac{\rho}{n} \frac{\partial q}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \lambda C \quad (8)$$

where q is the solid phase concentration (M/M); ρ is the soil bulk density (M/L³); n is the effective porosity (dimensionless); and λ is the 1st-order decay coefficient (T⁻¹).

When sorption and desorption follow the conventional linear model, the solid and aqueous phase concentrations can be related as:

$$q = K_{oc} f_{oc} C \quad (9)$$

Thus, the temporal differentiation of the solid phase concentration is:

$$\frac{\partial q}{\partial t} = K_{oc} f_{oc} \frac{\partial C}{\partial t} \quad (10)$$

When Equation 10 is plugged into Equation 8, the governing equation becomes:

$$\left(1 + \frac{\rho}{n} K_{oc} f_{oc}\right) \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \lambda C \quad (11)$$

When using the DED model to describe desorption, the correlation between the solid and aqueous phase concentrations is described with Equation 4. Differentiating the solid phase concentration q with regard to time yields:

$$\frac{\partial q}{\partial t} = \left(K_{oc}^{1st} f_{oc} + \frac{K_{oc}^{2nd} f_{oc} (q_{max}^{2nd})^2}{(q_{max}^{2nd} + K_{oc}^{2nd} f_{oc} C)^2} \right) \frac{\partial C}{\partial t} \quad (12)$$

When Equation 12 is plugged into Equation 8, the governing equation becomes:

$$\left[1 + \frac{\rho}{n} \left(K_{oc}^{1st} f_{oc} + \frac{K_{oc}^{2nd} f_{oc} (q_{max}^{2nd})^2}{(q_{max}^{2nd} + K_{oc}^{2nd} f_{oc} C)^2} \right)\right] \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \lambda C \quad (13)$$

Equation 13 can be easily solved with numerical approaches. The simplest numerical integration method is probably the Eulerian finite-difference method, which can be used with any spatial or temporal interpolation scheme (Remson, I., Hornberger, G.M. & Molz, F.J., 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 as:

$$\frac{\partial C}{\partial t} = \frac{C_x^{t+1} - C_x^t}{\Delta t} \quad (14)$$

where C_x^t and C_x^{t+1} are the concentrations of a solute at location x at two adjacent time steps –time step t and time step $t+1$, respectively. The first-order differentiation of concentration with respect to space is approximated by a central differencing scheme as:

$$\frac{\partial C}{\partial x} = \frac{C_{x+1}^t - C_{x-1}^t}{2\Delta x} \quad (15)$$

where C_{x+1}^t and C_{x-1}^t are the concentrations of a solute at time step t at location $x+1$ and $x-1$, respectively. The second-order differentiation of concentration with space is also approximated by the central differencing scheme:

$$\frac{\partial^2 C}{\partial x^2} = \frac{C_{x+1}^t - 2C_x^t + C_{x-1}^t}{(\Delta x)^2} \quad (16)$$

Therefore, the governing equation (Equation 13) can be expressed as:

$$\left[1 + \frac{\rho}{n} \left(K_{OC}^{1st} f_{OC} + \frac{K_{OC}^{2nd} f_{OC} (q_{max}^{2nd})^2}{(q_{max}^{2nd} + K_{OC}^{2nd} f_{OC} C_x^t)^2} \right) \right] \frac{C_x^{t+1} - C_x^t}{\Delta t}$$

$$= D \frac{C_{x+1}^t - 2C_x^t + C_{x-1}^t}{(\Delta x)^2} - v \frac{C_{x+1}^t - C_{x-1}^t}{2\Delta x} - \lambda C_x^t \quad (17)$$

Essentially, Equation 17 approximates derivatives (Equation 13) with differences by defining both spatial and temporal domains as discrete sections. The concentration of a solute at any time t and space x , C_x^t , can be solved with the concentrations at three adjacent nodes in the previous time step. For example, C_1^1 can be solved with C_0^0 , C_1^0 , and C_2^0 using Equation 17, and C_1^2 can be solved with C_0^1 , C_1^1 , and C_2^1 , and so on. Thus, once the initial conditions ($C_0^0, C_1^0, C_2^0, \dots, C_m^0$) and boundary conditions ($C_0^0, C_0^1, C_0^2, \dots, C_0^n$) are given, the concentration of a solute at any time t and space x can be calculated.

A few stability requirements have to be met because a difference equation cannot reasonably approximate a differential equation unless the spatial and temporal domains are sufficiently fine-discretized, i.e., Δx and Δt are sufficiently small. Zheng and Bennet (Zheng, C. & Bennett, G.D., 1995) stated that when dispersion and advection are solved simultaneously, such as in Equation 17, the stability criterion is:

$$\frac{2D \Delta t}{(\Delta x)^2} + \frac{v \Delta t}{\Delta x} \leq 1, \text{ or } \Delta t \leq \frac{(\Delta x)^2}{2D + v \Delta x} \quad (18)$$

DED-Transport – A Numerical Solute Transport Model

A screening-level solute transport model – “DED-Transport” – was developed based on Equation 17. The software is programmed in Excel/Visual Basic. It 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 post-remediation period, especially to evaluate the effects of bi-phasic 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:

- i) Post-remediation concentration changes in monitor wells in natural conditions;
- ii) Effect of pump and treat, simulated by increasing groundwater seepage velocity;
- iii) Effect of enhanced bioremediation, simulated by assigning a site-specific decay constant;
- iv) Effects of other mass removal mechanisms (e.g., air-sparging), simulated by assigning a lumped decay constant.

DED-Transport can also provide semi-quantitative results for some other remediation scenarios. For example, during in-situ oxidation (e.g., using permanganate), 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.

It is necessary to note that since DED-Transport is a screening-level model, it is not suitable to simulate some complex site conditions. For instance, if considerable amount of surfactants are used to accelerate mass removal, Equation 17, on which DED-Transport is based, needs to be modified. In this case, the "C" terms should be replaced by $C = C_w / (1 + K_{surf} \Gamma_{surf/w})$, where $\Gamma_{surf/w}$ (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} . Similarly, Equation 17 needs to be modified to account for the effects of significant amount of free phase contaminants, TPH, colloids, and cosolvents (Chen, W., et al, 2002). Nevertheless, since all these scenarios can be accounted for by modifying Equation 17, these remediation schemes can be simulated with codes similar to DED-Transport.

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 groundwater from upgradient 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.

Hydrogeological parameters:

- i) soil bulk density, ρ (kg/L);
- ii) aquifer effective porosity, n (dimensionless);
- iii) fractional organic carbon, f_{OC} (dimensionless); and
- iv) groundwater seepage velocity, v (ft/day)

Chemical-biochemical parameters:

- i) dispersion coefficient, D (ft²/day);
- ii) octanol-water partition coefficient, K_{OW} (L/kg);
- iii) aqueous solubility, C_{sat} (mg/L);
- iv) organic carbon normalized partition coefficient, K_{OC} (L/kg); and
- v) first-order decay coefficient, λ (day⁻¹)

Modeling parameters:

- i) inflow concentration, C_0 (mg/L) (typically $C_0 = 0$);
- ii) spatial dimension, X (ft); and
- iii) simulation time, T (day)

Note that D can either be input directly or by specifying an estimated plume length. The model uses the following equation to estimate D :

$$D = v \alpha_x \quad (19)$$

where α_x (ft) is the longitudinal dispersivity and is estimated using plume length, L_p (ft), as proposed by Xu and Eckstein (Xu, M. & Eckstein, Y.J., 1995):

$$\alpha_x = 3.28 \times 0.83 \left[\text{Log}_{10} \left(\frac{L_p}{3.28} \right) \right]^{2.414} \quad (20)$$

Similarly, a user has the option of inputting the half-life of the solute, $t_{1/2}$ (day), instead of λ . In this case, λ will be automatically calculated as:

$$\lambda = \frac{\text{Ln } 2}{t_{1/2}} \quad (21)$$

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.

As a screening-level model, DED-Transport assumes simplified initial and boundary conditions. For initial 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 flow path (i.e., C_0^0 , C_1^0 , C_2^0 , ..., C_m^0) assuming that concentration follows logarithmic distribution within the plume. The model assumes that the boundary condition (concentration in upgradient groundwater, i.e., C_0^0 , C_0^1 , C_0^2 , ..., C_0^n) 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.

The model output includes two graphs – the breakthrough curves, i.e., the concentration versus time at location X (e.g., Figure 5), and the concentration profile along the flow path (e.g., Figure 6). For example, Figure 5 includes two breakthrough curves observed at distance X assuming transport is controlled by:

- i) advection, dispersion, linear desorption, and 1st-order decay; and
- ii) advection, dispersion, dual-equilibrium desorption, and 1st-order decay.

Similarly, Figure 6 shows the concentration along the flow path assuming the transport is controlled by the above two mechanisms, respectively. In addition, the concentration-versus-time data at any location can be viewed in the two work sheets of the model.

DISCUSSION

The effect of dual-equilibrium desorption (DED) on soil and groundwater remediation can be understood with DED-Transport. 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 MCLs. 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 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 groundwater plumes. Studies of multiple fuel hydrocarbon sites have identified 17% of “exhausted” plumes in California (Rice, D.W., et al, 1995) and 11% in Texas (Mace, R.E., et al, 1997; Newell, C.J. & Connor, J., 1998), characterized by “insignificant temporal changes in length and mass with average plume concentrations not greater than 1 ppb,” despite of vigorous bioremediation processes. The presence of “exhausted” plumes is contradictory to the common fate and transport theories, because at such low concentrations it is unlikely that NAPL is still widespread at these sites, and commonly accepted BTEX biodegradation mechanisms do not include a low-concentration threshold where BTEX biodegradation shuts down.

The DED-Transport predictions, however, agree well with the presence of “exhausted” plumes. As discussed in the introduction section (Figure 1), desorption comprises two compartments, and after the initial repaired release from the 1st compartment, adsorbed contaminants are predominantly associated with the 2nd compartment. Because desorption from the 2nd compartment is controlled by a much larger partition coefficient, the mass release from the 2nd compartment is slow compared to the mass in the 2nd compartment. Thus, the slow desorption from the 2nd compartment serves as a continuing, low-concentration, yet long-term source to groundwater after other source materials (NAPL, desorption from the 1st compartment) are largely depleted. While remediation processes such as bioremediation and air-sparging may greatly facilitate mass removal from groundwater, 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 “exhausted” 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.

It is necessary to note that the DED effect on soil and groundwater 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-groundwater contaminations to be lesser problems than what would normally be expected (refer to 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 groundwater concentration estimated using the conventional approach (e.g., the linear model) would be approximately 0.25 mg/L, but in reality, the groundwater concentration is more likely to be 0.0012 mg/L (due to the DED effect), which is more than 200 times lower. To put another way, because the DED effect makes desorption very difficult, it may greatly reduce the risks of contaminated soils through leaching to groundwater. Thus, many affected sites may not even require active soil and groundwater remediation (refer to (Chen, W., et al, 2002)for detailed discussions).

Notation

α_x	longitudinal dispersivity (ft)
C	aqueous concentration (mg/L)
C_{sat}	aqueous solubility (mg/L)
C_x^t	concentration at location x and time step t
C_0	inflow concentration (mg/L)
C_{max}	maximum concentration within a plume (mg/L)
C_{min}	minimum concentration within a plume (mg/L)
D	hydrodynamic dispersion coefficient (L^2/T)
f	fraction of the 2 nd compartment saturated upon exposure (unitless)
f_{OC}	fractional organic carbon (unitless)
$K_{\text{OC}}^{1\text{st}}$	organic carbon normalized partition coefficient for the 1 st compartment (L/kg-OC)
$K_{\text{OC}}^{2\text{nd}}$	organic carbon normalized partition coefficient for the 2 nd compartment (L/kg-OC)
K_{OW}	octanol-water partition coefficient (L-water/L-octanol)
K_{surf}	partition coefficient to the surfactant (L/kg-surf)
λ	1st-order decay coefficient (T^{-1}).
L_p	plume length (ft)
n	soil effective porosity (dimensionless)
q	total sorption (mg/kg-soil)
$q^{1\text{st}}$	sorption to the 1 st compartment (mg/kg-soil)
$q^{2\text{nd}}$	sorption to the 2 nd compartment (mg/kg-soil)

$q_{\max}^{2\text{nd}}$	maximum sorption capacity of the 2 nd compartment (mg/kg-soil)
ρ	soil bulk density (M/L ³)
$r_{\text{surf/w}}$	mass of surfactant in the micellular form per liter of solution (kg-surf/L)
t	time (T)
Δt	temporal step in temporal discretization
$t_{1/2}$	half-life of the solute (day)
T	simulation time (day)
v	seepage velocity (L/T)
x	distance along groundwater flow direction (L)
Δx	spatial step in spatial discretization (L)
X	spatial dimension (ft)

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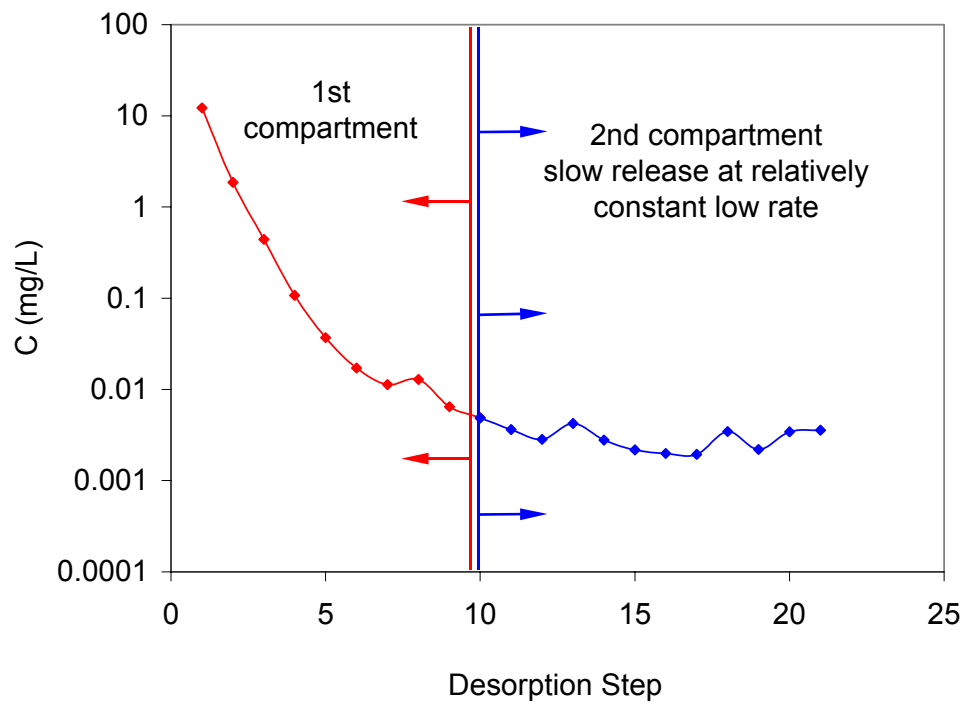


Figure 1. Plot of aqueous phase concentration versus desorption step (Kan et al., 1997). Repetitive desorption was conducted using naphthalene and Lula soil (0.27% OC). Extended desorption time was applied to the last two desorption steps – 19 days and 29 days, respectively.

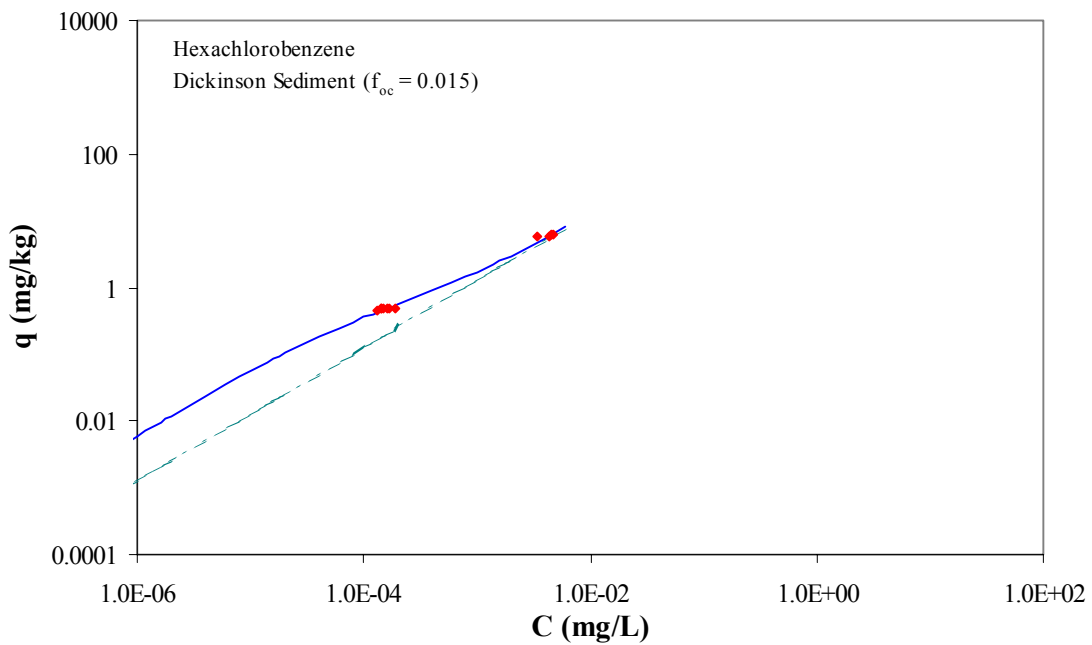
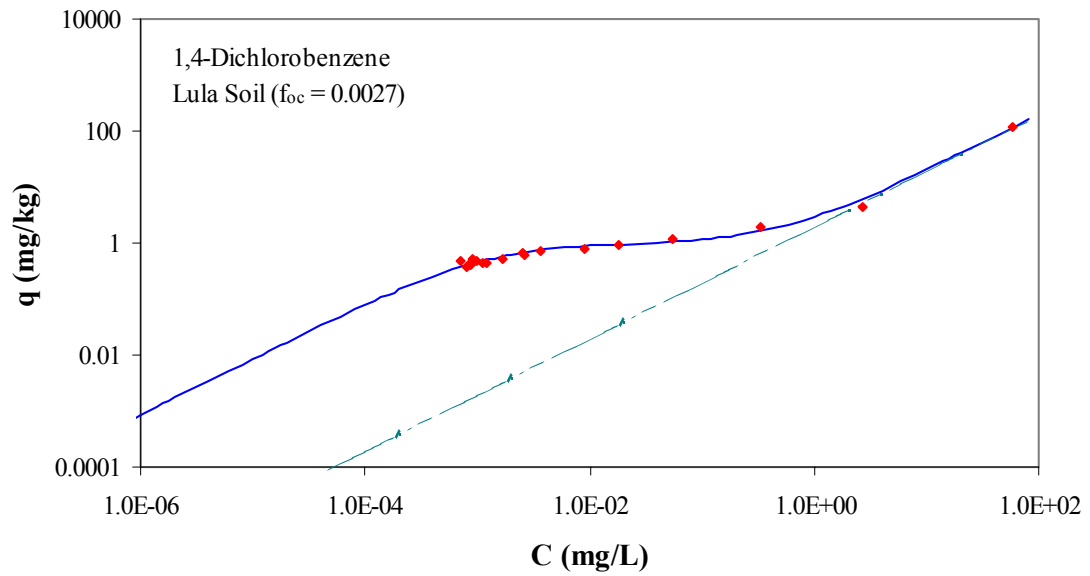


Figure 2. Plot of solid phase concentration versus aqueous phase concentration of model prediction and laboratory observations. Solid curve is the expected dual-equilibrium desorption curve and the dashed line is the expected linear desorption curve. The data points are experimental desorption results (Chen et al., 2000).

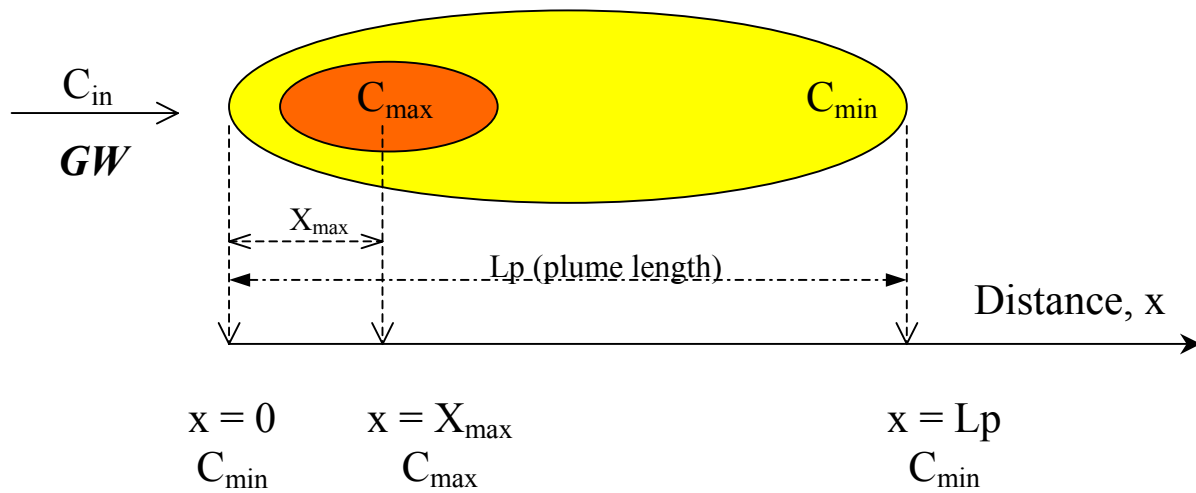


Figure 3. Illustration of the conceptual model of DED-Transport. A plume is defined by the maximum concentration, C_{max} , as well as the minimum concentration, C_{min} . Concentration at any location x along the flow pass is calculated from C_{max} and C_{min} assuming concentrations within the plume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

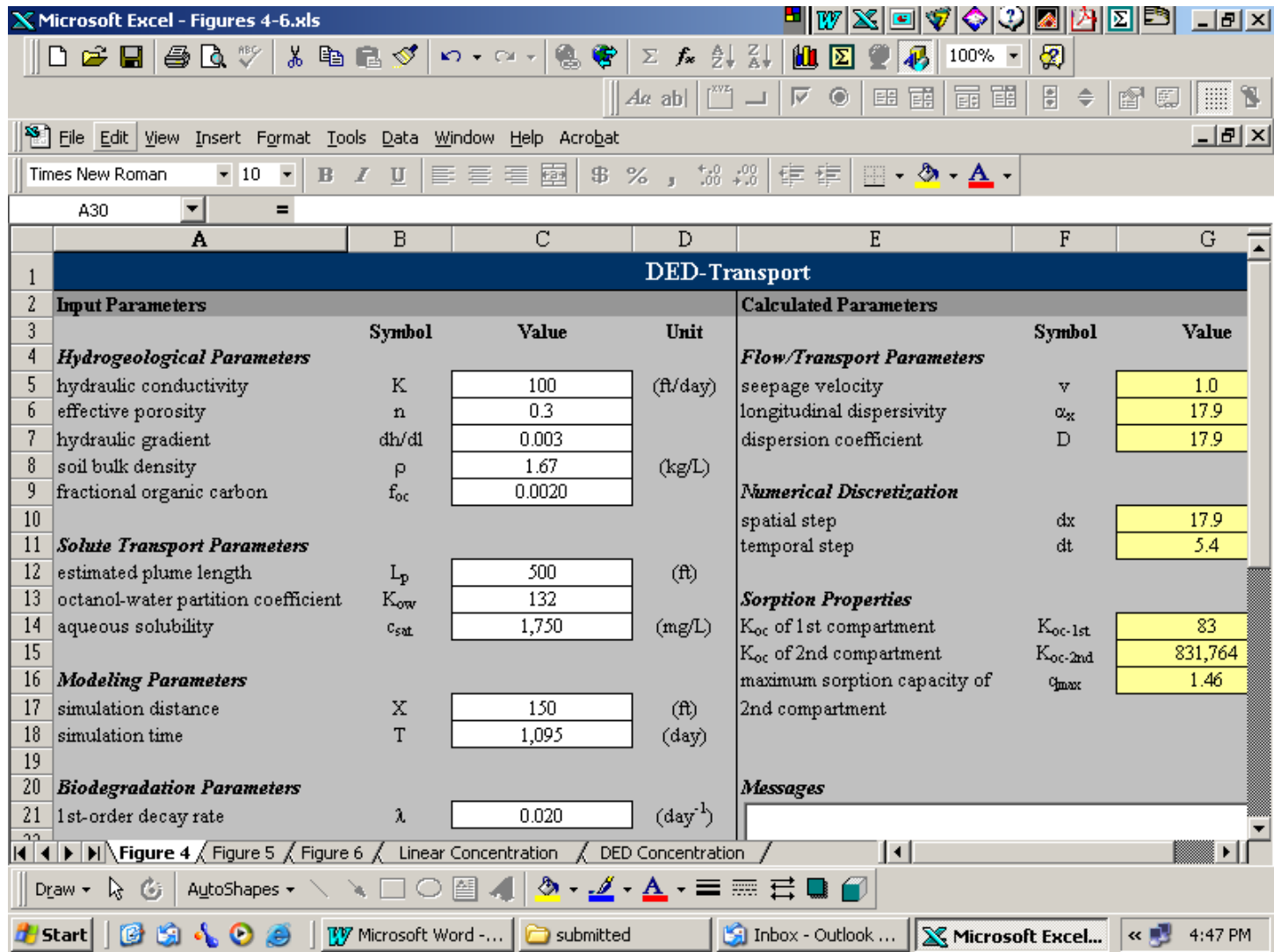


Figure 4. DED-Transport model input window. The left half of the window lists the site-specific and chemical-specific parameters. The right half lists modeling parameters typically generated by the software, but can be overwritten by a user.

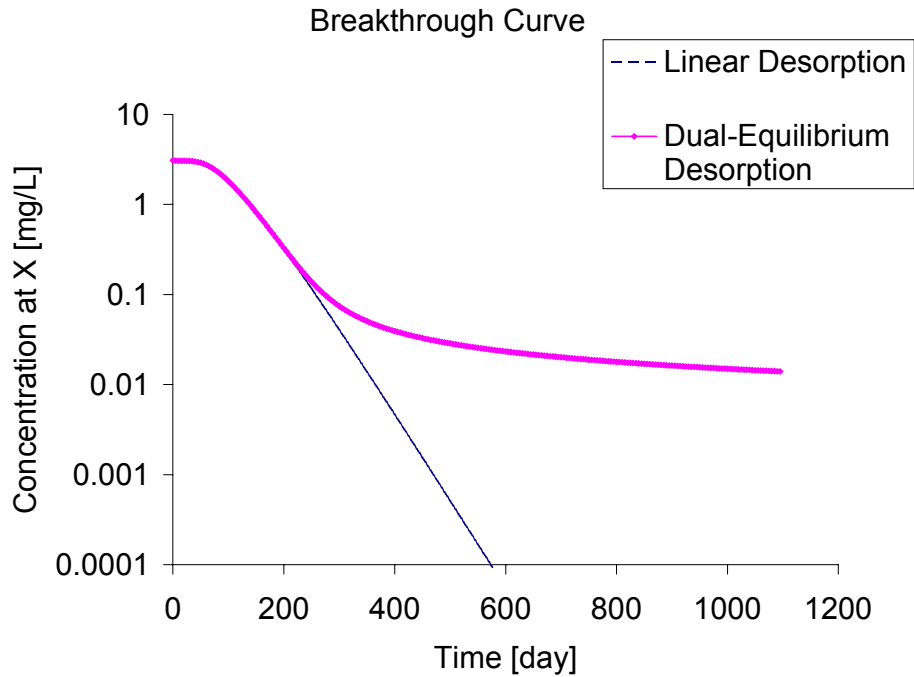


Figure 5. DED-Transport output graph – breakthrough curves at the simulation distance X. The two curves represent transport controlled by: 1) advection, dispersion, linear desorption, and 1st-order decay; and 2) advection, dispersion, dual-equilibrium desorption, and 1st-order decay.

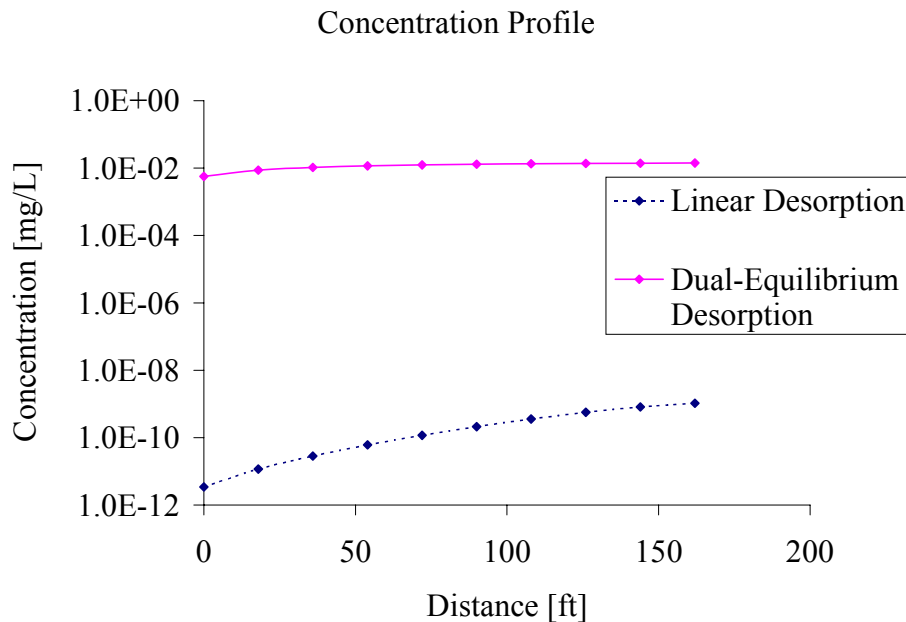


Figure 6. DED-Transport output graph – concentration profiles along the groundwater flow path in a plume at the simulation time T. The two curves represent transport controlled by: 1) advection, dispersion, linear desorption, and 1st-order decay; and 2) advection, dispersion, dual-equilibrium desorption, and 1st-order decay.