INDUCED DESORPTION OF DDT, DDD, AND DDE FROM A CONTAMINATED SEDIMENT

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ABSTRACT: Release profiles of p,p'-DDT, p,p'-DDD, and p,p'-DDE from sediment collected from Indian Creek, Alabama, were measured with a gas purge-induced desorption technique and compared to a model developed in this work. DDT entered this sediment via effluent discharged upstream from the collection site from 1947 to 1970 by a DDT manufacturing facility. The purge technique used vessels constructed with 70–100 μm fritted glass bottoms, through which air enters, distributing gas bubbles evenly to a sediment-water suspension. Purging compound from the water phase with the gas bubbles induced desorption of compound from the sediment particles. The purged chemicals were captured on tenax traps. Purge experiments were performed with sediment masses ranging from 0.37 to 3.7 g in 200 mL water at an air flow rate of 1 L/min. The total percentage removal of each compound after 46 days averaged 22, 58, and 75% for DDT, DDD, and DDE, respectively, indicating the extreme resistance of DDT to desorption from this sediment. The time to reach 25% removal was approximately 50 days for DDT and 4 days for DDD. Results are compared to a simple Fickian diffusion model in which diffusion is assumed to occur in one direction from a fixed depth to a plane surface. The concentration at the exposed surface is assumed to be in equilibrium with the aqueous concentration, which in turn is depleted by transfer to the gas phase through first-order decay. Simulations indicate that DDD transfer across the liquid-gas interface is limiting at high sediment concentrations.

INTRODUCTION

Sorption affects the transport, bioavailability, and chemical reactivity of virtually all anthropogenic and natural compounds in the environment. It is most significant for low water solubility compounds such as DDT and the polychlorinated biphenyls (PCBs), promoting their extreme environmental persistence (Di Toro et al. 1982). For these very hydrophobic compounds, sorption to soils and sediments is often kinetically limited with respect to other environmental fate and transport processes. Consequently, several quantitative kinetic models have been developed (Karickhoff and Morris 1985; Miller and Weber 1986; Rao et al. 1979; Wu and Gschend 1986). Some have been incorporated into comprehensive fate and transport models for calculating environmental exposure concentrations.

Within kinetic models, different phenomenological descriptions of the sorption process and geometrical descriptions of the sorptive matrix have been advanced to characterize mass transfer. These descriptions range in complexity, although by prerequisite are empirical due to the heterogeneity of natural soil materials. Descriptions of mass transfer in these models include 1) Simple first-order mass transfer between the bulk aqueous and sediment phases; 2) first-order mass transfer to a portion of the sediment sorptive sites with the remaining portion in equilibrium with the aqueous phase (i.e., a two-box model); 3) unidirectional (i.e., 1D) diffusion to or from a plane surface exposed to the aqueous phase; and 4) diffusion in spherical coordinates within aggregate particle pores.

Data to calibrate or assess these models often has been obtained from experiments in which sediment solutions are purged with gas to induce desorption from the particles. This method is particularly applicable to highly sorbing compounds. Karickhoff and Morris (1985), for example, examined the desorption of selected chlorobenzenes, pyrene, and trifluralin, and Coates and Elzerman (1986) investigated desorption of PCBs. More recently, Koelmans et al. (1993) investigated the desorption of chlorobenzenes from various phytoplankton using a gas purge method.

In early experiments, Karickhoff and Morris (1985) made the perceptive observation that the cumulative purge-induced removed fraction of sorbed chemical was a linear function of the square root of purge time, in some cases for up to 60% release. This type of release profile is consistent with Fickian diffusion occurring from a semiinfinite source to a plane surface depleted of the chemical. They showed this to be the case by invoking constant solute concentrations at parallel slab surfaces as boundary conditions to Fick's second law (or the heat equation) in one dimension, which results in the following as an approximate solution at early time periods (Crank 1975):

$$\frac{M_t}{M_\infty} = \frac{4}{\pi^{0.5}} \left(\frac{Dt}{L^2}\right)^{0.5} \tag{1}$$

where t = time (min); M_t = the total mass of solute which has left the source at t; M_∞ = the mass of solute that has been released at infinite time, D = the diffusion coefficient (cm^2/s); and L = the thickness of the source (cm). M_t/M_∞ ($=f_t$) = fraction of the total mass released at t. Karickhoff and Morris referred to the product of all the constants on the right side of (1) as the diffusive transport coefficient, k. This value can be determined by regressing the fraction released versus the square root of time

$$f_t = k\sqrt{t} \tag{2}$$

This model is very attractive because it accurately represents the experimental data and is extremely simple. As with many other simple models, however, its ability to "predict" rather than simply represent experimental data is limited. Other factors such as organic carbon content are not taken explicitly into account and the boundary conditions are of limited value for modeling natural or engineered systems.

To alleviate these limitations, we have implemented in this research new boundary conditions to this simple model of one-dimensional (1D) Fickian diffusion. These new boundary conditions allow for a more thorough interpretation of the experimental data, and with only slight modification, allow for easy incorporation of the model and the experimentally

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for easy incorporation of the model and the experimentally determined parameters into more comprehensive transport models. The experimental data we have modeled is gas purge-induced desorption profiles of 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT) and its initial degradation products, 2,2-bis(4-chlorophenyl)-1,1-dichloroethane (DDD), and 2,2-bis(4-chlorophenyl)-1,1-dichloroethylene (DDE) from sediment suspensions. By invoking these new boundary conditions and solving with numerical methods, concentration profiles or gradients within sediment particles may be estimated, and the effect of preexisting gradients on model calculations may be examined.

The new boundary conditions require definition of the matrix through which molecular diffusion occurs. For simplicity, we assume that the limitation to mass transfer within the soil aggregates results from molecular diffusion within the organic fraction of the sediment. This assumption is quite different from that used by other researchers; for example, Wu and Gschwend (1986) have assumed that resistance to mass transfer is dominated by diffusion within pores of spherical soil aggregates, with local sorption equilibrium assumed between the intraaggregate pore water and the adjacent organic matrix. In reality, both processes (i.e., pore and matrix diffusion) as well as other processes may limit mass transfer. Separately, both approaches are compatible with the thermodynamic concept that hydrophobic compounds are "solvated" by the organic matrix within soils (Chiou et al. 1979). Further, for the same geometrical shape or shapes, both models will provide the exact same mathematical result, because in each only one diffusional resistant to mass transfer is assumed. We may compare the general shape of model curves to our experimental results using either model construct and easily draw inferences for the other.

SLAB DIFFUSION MODEL

The control volume of idealized soil organic material is depicted in Fig. 1 as having parallel surfaces of area, a, separated from each other by the diffusive path length, L. The surface areas, represented in Fig. 1 as opposing circles, may take any geometry where the internal boundary is an isolated surface at distance $x = L$, equidistant at all points from the external surface at $x = 0$ exposed to the water phase. The external surface may be noncontiguous, which is the case for a collection of particles. Diffusion in this matrix is modeled with Fick's second law that describes 1D molecular diffusion in an isotropic media

$$\frac{\partial \mu}{\partial t} = D \frac{\partial^2 \mu}{\partial x^2} \tag{3}$$

where μ = concentration of compound (mol/cm^3 matrix); and again D = the diffusion coefficient (cm^2/s). Boundary conditions are defined at the isolated internal boundary, and at the external surface after appropriate assumptions.

Assuming an isolated internal boundary at $x = L$ provides the same mathematical result as assuming that both surfaces are exposed to the water phase, provided that the exposed surface area and volume remain constant, and in the case of the isolate internal boundary, no gradient in chemical concentration is allowed to develop at this boundary

$$\left.\frac{\partial \mu}{\partial x}\right|_{x=L} = 0 \tag{4}$$

This boundary condition does not prevent loss of compound from the isolated internal boundary; it only requires that the concentration gradient at this point equal zero to prevent diffusion across the boundary.

The boundary condition accounting for mass transfer across

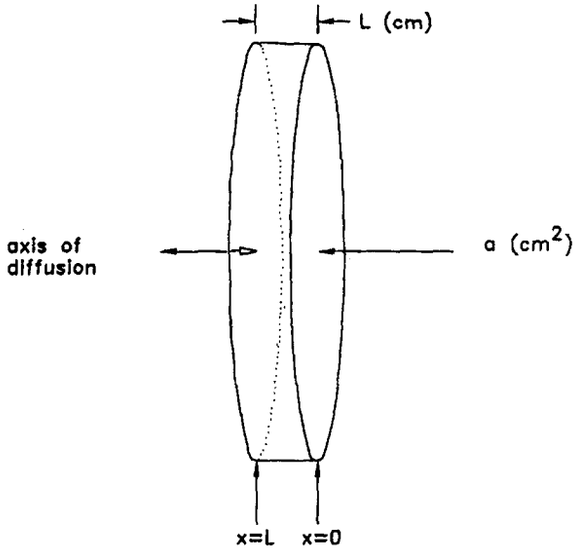

FIG. 1. Idealized Control Volume

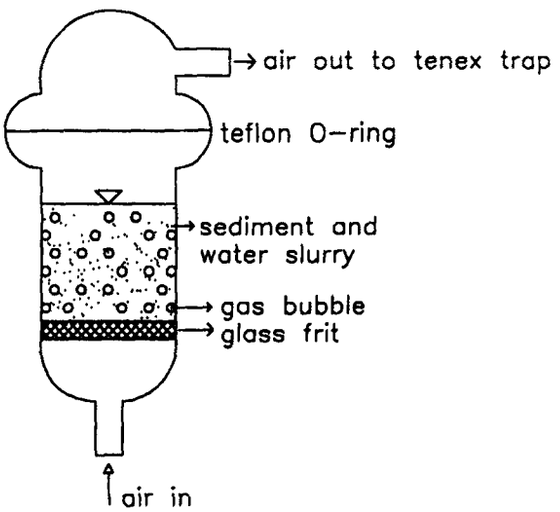

FIG. 2. Purge Vessel Schematic; Total Volume Is Approximately 300 mL

the external surface-water interface may be deduced from the chemical mass balance around the liquid phase. The liquid phase is depicted in Fig. 2 as a portion of the slurry that also contains sediment particles and gas bubbles. Mass is transferred from the liquid phase to the gas phase by continuous purging, depleting the aqueous phase of chemical. In turn, the solid phase is depleted via transfer to the liquid phase. Assuming mass transfer from the liquid to the gas phase is limiting, the general mass balance for the liquid phase becomes

$$V_L \frac{dC_{aq}}{dt} = DA \left.\frac{\partial \mu}{\partial x}\right|_{x=0} - k_g V_L \left(C_{aq} - \frac{C_g}{m}\right) \tag{5}$$

where C_g = solute concentration in the gas phase (mol/mL); C_{aq} = solute concentration in the aqueous phase (mol/mL); V_L = liquid volume (mL); k_g = mass transfer coefficient (s^{-1}); and m = Henry's Law constant [(mol/mL air)/(mol/mL water)]. The accumulation term in this equation is negligible because mass flux from the solid to liquid and from liquid to gas is very large compared to accumulation in the liquid phase. We also assume that the bulk gas phase cocentration is zero due to the short retention time of the bubbles in the reactor (<1 s)

$$\left.\frac{\partial \mu}{\partial x}\right|_{x=0} = \frac{k_g V_L}{DA} C_{aq} \tag{6}$$

Finally, a mathematical relationship between μ and C_{aq} exists if local equilibrium conditions are assumed at the solid-water interface. Because sorption occurs predominantly to the organic phase of the sediment, C_{aq} may be defined by

$$C_{aq} = \frac{C_s|_{x=0}}{K_{oc} f_{oc}} \tag{7}$$

where C_s = solute concentration on the particles (mol/g); K_{oc} = organic carbon normalized partition coefficient (mL/g); and f_{oc} = fraction organic carbon (g/g). Recall, we assume diffusion occurs within the organic matrix of the solid phase. Thus, the slab represents the volume of organic material in the sediment and μ has units of compound per organic matter (mol/cm^3). It is defined by (8) for any location within the slab

$$\mu = \frac{C_s \rho_h}{f_{oc}} \tag{8}$$

where ρ_h = density of the organic carbon within the organic matter (g/cm^3). Combining (6)–(8) yields (9) as the second boundary condition

$$\left.\frac{\partial \mu}{\partial x}\right|_{x=0} = \frac{V_L k_g}{DAK_{oc}\rho_h} \mu|_{x=0} \tag{9}$$

The final system of equations [(3), (4), and (9)] has no known analytical solution; therefore, the equations were solved by finite differences with both explicit and Crank-Nicholson numerical methods. Both solutions were developed to confirm computational accuracy.

For cohesive sediments, that is, sediments with high organic carbon contents and/or a large amount of swelling clays, Karickhoff and Morris (1985) found that the diffusive transport coefficient, k, of (2) was inversely proportional to the solids concentration. For these sediments, k increases upon addition of a dispersant. It was concluded that this effect was the result of the dissociation of sediment aggregates at low solids concentrations, essentially reducing diffusional path lengths. At higher concentrations, particles would be more likely to reaggregate. For less cohesive sediments with less organic carbon, the effect was minimal. Alternatively, a similar solids concentration effect would result, even for noncohesive soils, if mass transfer to the gas phase was restricted. Resistance to mass transfer across the water-gas interface may produce a significant aqueous phase solute concentration, effectively decreasing the concentration gradient through the particles. This effect likely would be most evident for compounds with very low water solubilities and low vapor pressures.

EXPERIMENTAL METHODS

Chemicals and Reagents

Analytical standards of 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT or p,p′-DDT), 2,2-bis(4-chlorophenyl)-1,1-dichloroethane (DDD or p,p′-DDD), and 2,2-bis(4-chlorophenyl)-1,1-dichloroethylene (DDE or p,p′-DDE) were prepared in isooctane from the solid materials purchased from Aldrich Chemical Company, with purities greater than 98%. HPLC grade acetone, isooctane, and acetonitrile were purchased from Fischer Scientific and Alltech Associates, Inc. Water for all experiments was deionized and purified further through a Barnstead Nanopure system. Tenax resin (35/60 mesh, TA) was purchased from Supelco, Inc.

The sediment was from the Huntsville Spring Branch-Indian Creek stream system in the Wheeler National Wildlife Refuge on the Redstone Army Arsenal near Huntsville, Alabama, and supplied to us from the United States EPA research laboratory in Duluth, Minnesota. The sample was a subsample of a larger composite of three separate Ponar grabs. It was stored at 4°C, including during transportation, until used. A DDT manufacturing facility, located upstream from the sample collection site, discharged effluent into the stream from 1947 to 1970 (Hoke et al. 1994). The sample contained 76.4% dry solids and 0.6% organic carbon. Upon visual inspection, the sediment is noncohesive.

Purge Apparatus

The complete purge apparatus is shown in Fig. 3. The apparatus uses laboratory air, purified through drierite and activated carbon columns, supplied to the system with an oilless

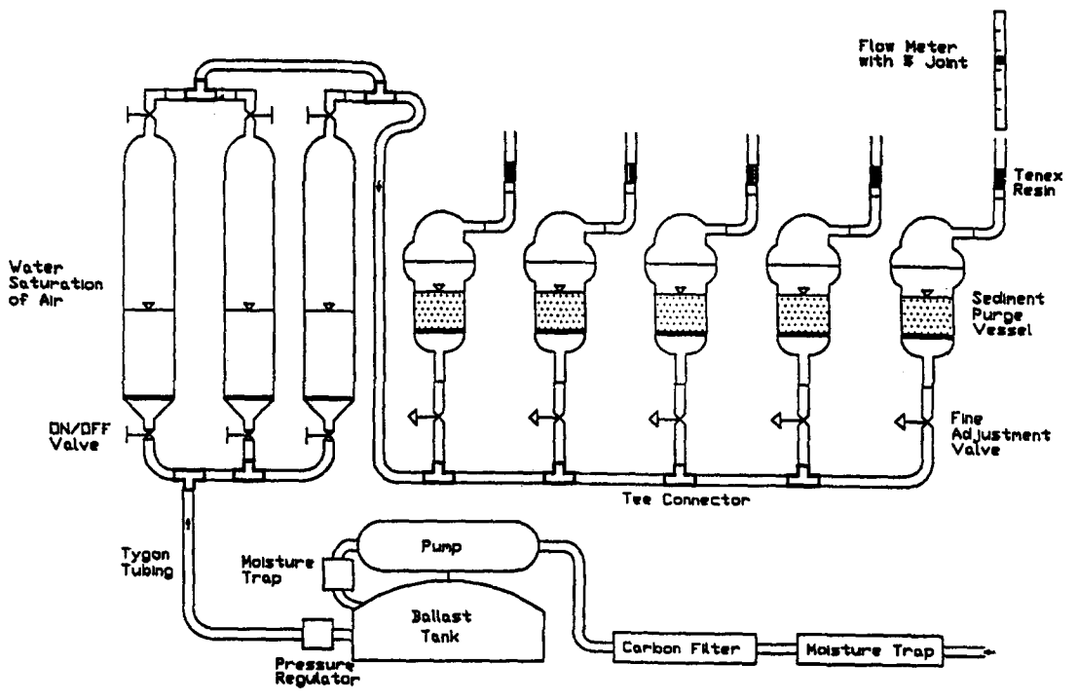

FIG. 3. Experimental Apparatus

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compressor and ballast tank (Thomas Industries, Inc., Model CMD-75). A pressure regulator following the ballast tank maintains a constant 10 psi to the system. From the ballast tank, air flows through a tenax trap and through distilled water columns to resaturate before flowing to the purge vessels. Each purge vessel (Ace Glass Incorporated) is preceded by a fine adjustment stopcock to regulate gas flow. Each vessel has a 70–100 μm fritted glass bottom through which the air enters to distribute the gas bubbles evenly to the sediment-water suspension. The top of each vessel is clamped to the bottom with a teflon o-ring seal. The air exits at the top of each reactor and is forced through a tenax trap to capture the purged compounds. Ground glass fittings on these traps allow for periodic attachment of a flow meter (Gilmont Instruments, Inc.).

Determination of Model Parameters

A number of parameters were independently determined, either experimentally or by estimation methods. Only the diffusive path length, L, which is the same for each compound, and diffusivity, D, which is specific to each compound, were used as adjustable parameters to obtain the most reasonable model simulations of the experimental data.

The organic carbon density in sediment humic material was calculated based on the humic molecular structure of $C_{10}H_{13}O_5N_9$ (Schnitzer and Khan 1972) and the volume occupied by each element (Fuller et al. 1966) to be 0.6 g/cm^3 organic matter. The organic carbon content of the sediment was experimentally determined, and K_{oc} was estimated from the octanol-water partition coefficient, K_{ow}, assuming $K_{oc} \approx 0.5K_{ow}$ (Hassett et al. 1980; Karickhoff 1980 and 1981).

Determination of k_g

The value of k_g for each compound was determined by purging distilled water solutions containing each compound separately at a designed flow rate of 1 L/min. A complication arises in that a significant amount of each compound partitions to the reactor glass in the absence of the sediment. This amount was accounted for by assuming rapid partitioning to the glass. For each distilled water experiment, the change in the total concentration in the purge vessel with time is expressed as

$$\frac{dC_t}{dt} = -k_g C_{aq} \tag{10}$$

where C_t = total concentration (M); C_{aq} = aqueous phase concentration (M); k_g = mass transfer coefficient (s^{-1}). The equilibrium equation describing partitioning to the wall and the associated mass balance equation are given by (11) and (12), respectively

$$K_{\text{wall}} = \frac{C_{\text{wall}}}{C_{aq}}; \quad C_t = C_{\text{wall}} + C_{aq} \tag{11, 12}$$

where C_{wall} = the concentration on the wall normalized to the reactor volume (mol/L). Equations (10)–(12) may be combined

$$\frac{dC_t}{dt} = \frac{-k_g}{(1 + K_{\text{wall}})} C_t \tag{13}$$

rearranged and integrated

$$\ln C_t = \ln C_{t=0} - \frac{k_g}{1 + K_{\text{wall}}} t \tag{14}$$

Regression of ln C_t (abscissa) versus time (ordinate) results in a slope = $k_g/(1 + K_{\text{wall}})$ from which values of k_g were determined.

For these measurements, stock solutions were prepared by plating a quantity of test compound onto the walls of a 1-L volumetric flask through evaporation of the isooctane carrier, resulting in approximately one half the solubility of each compound in 1 L. The aqueous concentrations in these solutions were determined by extracting 200-mL samples with 2-mL isooctane followed by gas chromatography (GC) analysis of the isooctane. From the remaining 800 mL, a 200-mL aliquot was placed in a purge vessel. A 5-mL sample was removed and extracted, providing the initial datum point at $t = 0$. The remaining solution was purged with air at 1 L/minute. Subsamples of 5 mL were removed periodically, rinsing the transfer pipette with 1 mL of acetonitrile. The subsamples were extracted with 0.5 mL isooctane prior to GC analysis. Upon termination of a purge, the remaining water was collected, and the purge apparatus was rinsed with approximately 5–7 mL of acetonitrile to remove any remaining compound. The water and acetonitrile were extracted with 2 mL of isooctane for GC analysis.

Initial Compound Concentrations

The initial DDT, DDE, and DDD concentrations within the sediment were determined in triplicate independently of purge experiments. For each sample, approximately 0.5 g of wet sediment was weighed into a 40-mL test tube fitted with a teflon cap. Acetone (10 mL) was added and the mixture was vortexed for two min. Each sample was placed in an ice bath and sonicated for 20 min with a Fischer Scientific F50 microprobe sonicator at approximately 20 W. To each sample, 5 mL of water, 5 mL of isooctane, and an additional 15 mL of water were added. Samples were vortexed for five minutes. To improve phase separation, samples were centrifuged for five min at 5,000 rpm in a Sorvall RC-2B ultracentrifuge. The isooctane layers were removed and analyzed by GC methods. Compound concentrations were referenced to sediment dry weight by independently determining the sediment moisture content.

Sediment Purge Experiments

For each sediment purge experiment, a predetermined mass of sediment was placed into a 250-mL glass flask. Approximately 10 mL water was added to the sediment in increments of 1–2 mL, mixing after each addition. Any large sediment aggregates were crushed to improve the uniformity of the sample. Additional water was added, resulting in a total aqueous volume of 200 mL and the sample was transferred to a purge vessel. Samples were purged for 46 days during which time tenax resins were removed and eluted periodically. Upon removal, a new tenax trap was installed immediately. Compounds were eluted from each tenax trap with three 5-mL serial additions of acetone. The acetone was evaporated and 2 mL isooctane were added and vortexed prior to analysis by GC.

Upon discontinuation of an experiment, the reactor vessel and its contents were extracted to determine residual DDT, DDD, and DDE. The slurry was removed and the vessel was rinsed with 20 mL acetonitrile. An additional 5 mL of acetonitrile were forced through the frit with nitrogen gas. These solutions were combined and sonicated in an ice bath for 10 min and extracted with 3 mL isooctane.

Chemical Analysis

All samples were analyzed by splitless injection onto a Hewlett Packard 5890 Series II GC equipped with an electron capture detector, and a fused silica 28 m × 0.323 mm DB-5 capillary column (J & W Scientific). The oven temperature was ramped from 175°C (for 3 min) at a rate of 10°C/min, to 250°C (for 4 min). The carrier gas was helium. Sample reten-

tion times and areas were compared to those of analytical standards. For similar samples from the Huntsville site, Hoke et al. (1994) chromatographically separated para-para isomers from ortho-para isomers for each compound and reported that the ortho-para isomers may constitute from zero (DDT) to 20% (DDE) of the total. On our chromatographs, a peak always appeared 0.2 min after the p,p'-DDE peak, presumably due to o,p'-DDE; however, the identities of this and several other unknown peaks were not confirmed.

RESULTS AND COMMENTS

k_g Determination

The results of experiments in which individual compounds were purged from distilled water are shown in Fig. 4. In this figure, the amount of each compound remaining in the purge vessel ($C_{aq} + C_{wall}$) is plotted versus time. The values of K_{wall} for DDT and DDD were calculated from the values of C_{aq} and C_t at the termination of each purge to be 0.31 and 0.11, respectively (dimensionless units). The final elution of DDE yielded an unreasonably high value for K_{wall}; therefore, a two-parameter fit to all the data was performed. Varying K_{wall} from 0.1 to 1.0 resulted in visually straight line regressions of ln C_t versus time with corresponding k_g values of 4.7×10^{-4} to 5.7×10^{-4} s^{-1}. As this range is small, K_{wall} was "set" to 0.5, resulting in a k_g value of 5.2×10^{-4} s^{-1}. This value, while of the same order of magnitude as the values for DDT and DDD of 3.8×10^{-4} s^{-1} and 2.5×10^{-4} s^{-1}, respectively, is slightly higher.

Sediment Experiments

The initial concentration of each compound on the sediment was measured with the acetone extraction method and the sediment purge mass balance method, both previously described. The average concentrations of the para-para isomers of DDT, DDD, and DDE were 16.1 ± 0.16, 16.3 ± 0.16, and 4.22 ± 1.0 nmol/g dry sediment, respectively.

For each purge experiment, the data obtained were simply the number of moles of each compound released to the gas phase between each tenax trap replacements. As each purge vessel had different sediment concentrations, the data are reported in Fig. 5(a) as the cumulative moles recovered per gram dry-weight sediment (r/m) at the corresponding sampling time. Table 1 lists the sediment mass used in each purge experiment (numbered 1–4). The flow rate of 1 L/min was the same as that for determining k_g. Purges 1 and 2, with 0.373 g and 0.387 g, respectively, demonstrate experimental reproducibility. Purge 2 removal was consistent with purge 1 removal, resulting in a difference after 46 days of approximately 15–20% for each compound between purges. Recall the cumulative nature of the data and note that the gaps between the data sets do not spread significantly at longer purge times.

For DDD and DDE, approximately 50% of the total compound mass was removed within the first 10 days. For these data (days 1–10), fractional releases (r/m) plotted versus the square root of time result in linear plots. For purges 1 and 2, r/m ratios plotted versus the square root of time for the entire time period result in concaved plots towards the abscissa for DDD and DDE, and convex plots toward the abscissa for DDT. For DDD and DDE this trend appears to be consistent with the depletion of chemical from the internal boundary; however, model predictions indicate removal remains linear as a function of square root of time up to about 80% removal. The opposite trend by DDT (in the same particles) may result from either nonuniform initial concentration profiles within the particles, or extensive sorption to sediment materials (e.g., clays or condensed organic carbon) that are more highly resistant to diffusion. The total percentage removal of each compound at day 46 is provided in Table 1 and averages 22, 58, and 75% for DDT, DDD, and DDE, respectively.

Included in Fig. 5(a) are model results using coefficients reported in Table 2. Additionally, $\mu_{x=0-L}$ at $t = 0$ is assumed constant through the slab ($=\mu_o$), and calculated using (8) where C_s is the measured average initial concentration. L and D were used as fitting parameters, with L (=3 μm) invariant among the compounds and purge experiments, and D invariant for each compound among the experiments. The estimated values for D are in general agreement with those estimated by Karickhoff and Morris (1985) of approximation 10^{-13} cm^2/s for hexachlorobenzene (log K_{ow} = 5.5) in sediments assuming 5 μm radius spheres. Results are reported only for purge 1 and 4 simulations, as these cover the extremes in the experimental sediment concentrations. For DDT and DDE, the simulations are virtually independent of the sediment concentration exemplified by the infinite depth planar source model in which compound is fully depleted at the exposed surface at all times. The associated concentration profiles of μ/μ_o versus distance within the 3 μm slab, shown in Fig. 5(b) for purge 4, indicate this effect. Depletion at the surface is even more evident in purge 1, 2, and 3 simulations, as purge 4 contained the largest amount of sediment. These profiles also indicate that after day nine, the model predicts extensive depletion of DDE at the internal boundary, whereas for DDT no depletion occurs during the 45 days of simulation.

The experimental data and the simulations for DDD indicate a dependency on sediment concentration. Recall, this dependency may result from changing or altered mass transfer resistances, such as increased diffusional path lengths due to sediment cohesion, and/or significant water-air mass transfer resistances. In our experiments, the same sediment contains all three compounds, yet this trend occurs only for DDD, suggesting the latter as a possible explanation. This trend is grossly predicted with the model by adjusting D and L, which by themselves do not control mass transfer across either the gas-water or sediment-water interface. The simulated concentration profiles of DDD for purge 4 [Fig. 5(b)] indicate depletion from the surface is more limiting than for DDT or DDE.

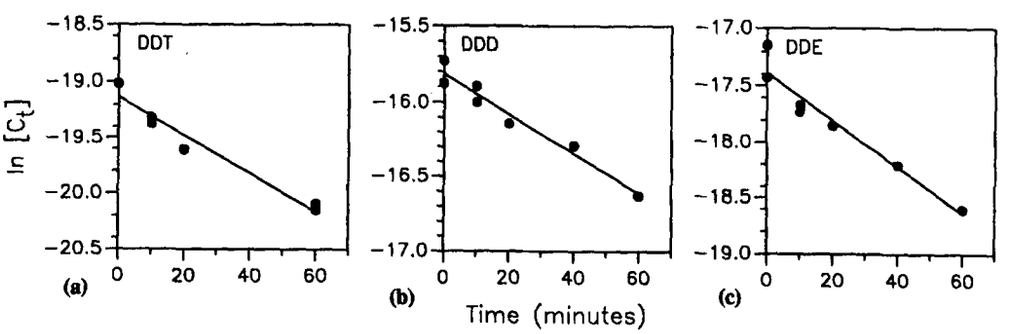

FIG. 4. Loss of Each Compound from Distilled Water upon Purging with Air at 1.0 L/min

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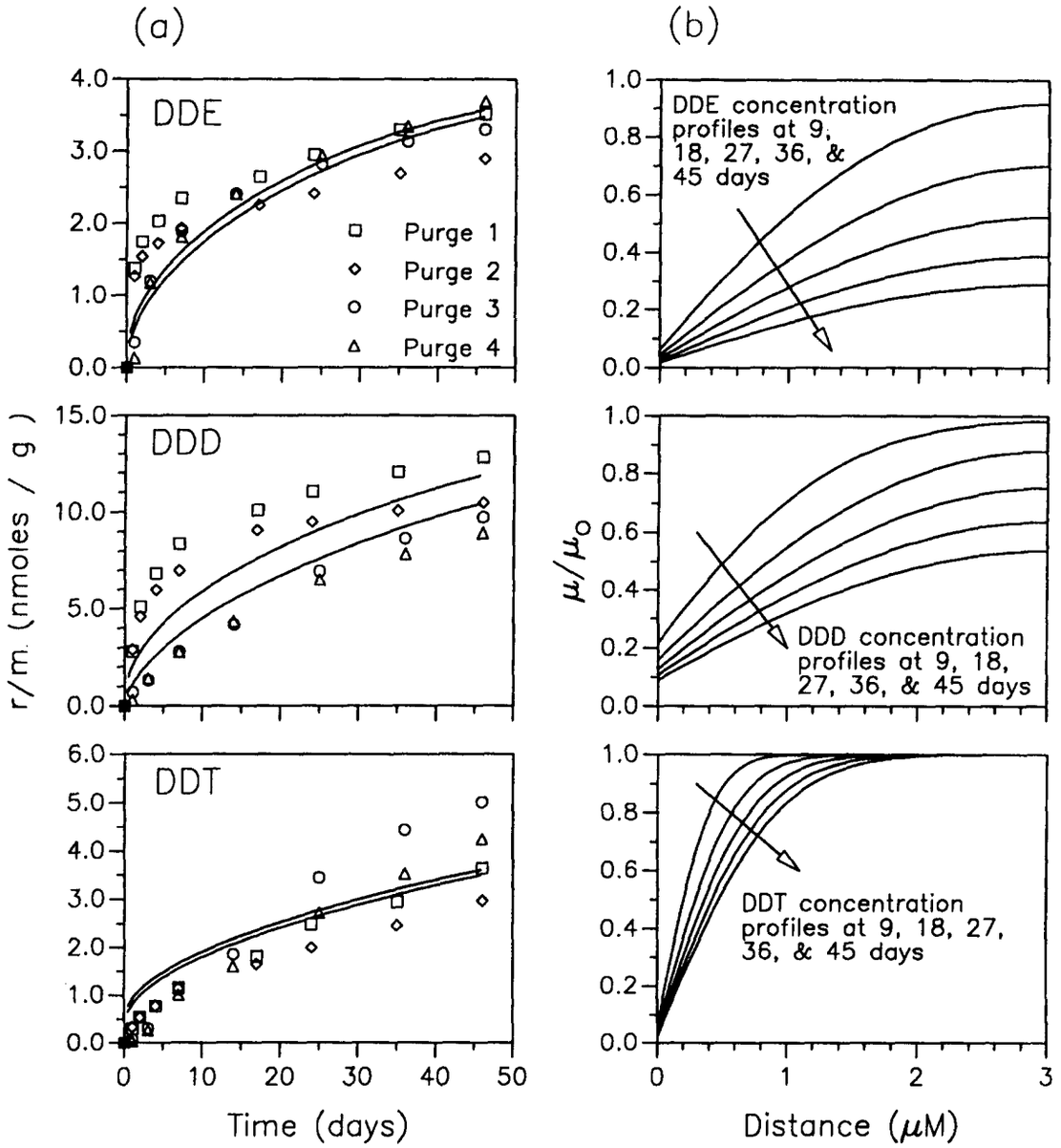

FIG. 5. (a) Purge 1–4 Data and Simulations for Purge 1 (Top Line) and Purge 4 (Bottom Line); (b) Concentration Gradients Calculated for Purge 4 at 9-Day Intervals

TABLE 1. Experimental Conditions and Mass Recovered

Purge (1)	Sediment mass (g) (2)	Flow rate (L/min) (3)	Cumulative Percent Removed at Day 46		
			DDT (4)	DDD (5)	DDE (6)
1	0.373	1.0	22%	65%	83%
2	0.387	1.0	19%	65%	69%
3	1.97	1.0	23%	45%	59%
4	3.74	1.0	23%	55%	87%

TABLE 2. Model Coefficients

Compound (1)	log K_{ow}[a] (2)	D (cm²/s) (3)	k_g (s^{-1}) (4)
DDT	6.84	7×10^{-16}	3.77×10^{-4}
DDD	6.7	1×10^{-14}	2.47×10^{-4}
DDE	6.36	1.5×10^{-14}	5.23×10^{-4}

Note: For all compounds, $\rho = 0.6$ g/mL; $f_{oc} = 0.006$; $L = 3$ μm; and $V_T = 200$ mL.
[a]Estimated from SPARC (Karickhoff et al. 1989).

Simulation concentration profiles of purges 1 and 2 indicated depletion from the surface may be assumed for all compounds.

The simplicity of the empirical model suggests that more accurate predictions are possible by inclusion of other model elements or terms. The most obvious extension is to include slabs of different diffusional lengths, similar to the approach taken by Wu and Gschwend (1986) in simulating mass transfer within spherical particles of different radii. However, the discrepancies between the data and the simulations occur in opposite directions among the compounds, particularly between DDT and DDE. For all purges, the model overpredicts the initial loss of DDT and underpredicts the initial loss of DDE. Inclusion of more "slabs" would not improve simulations among the compounds. Hence, it becomes necessary to examine other factors which may contribute to the experimental phenomenon.

DDD and DDE are decay products of DDT, hence the average sediment exposure time to these products is less than

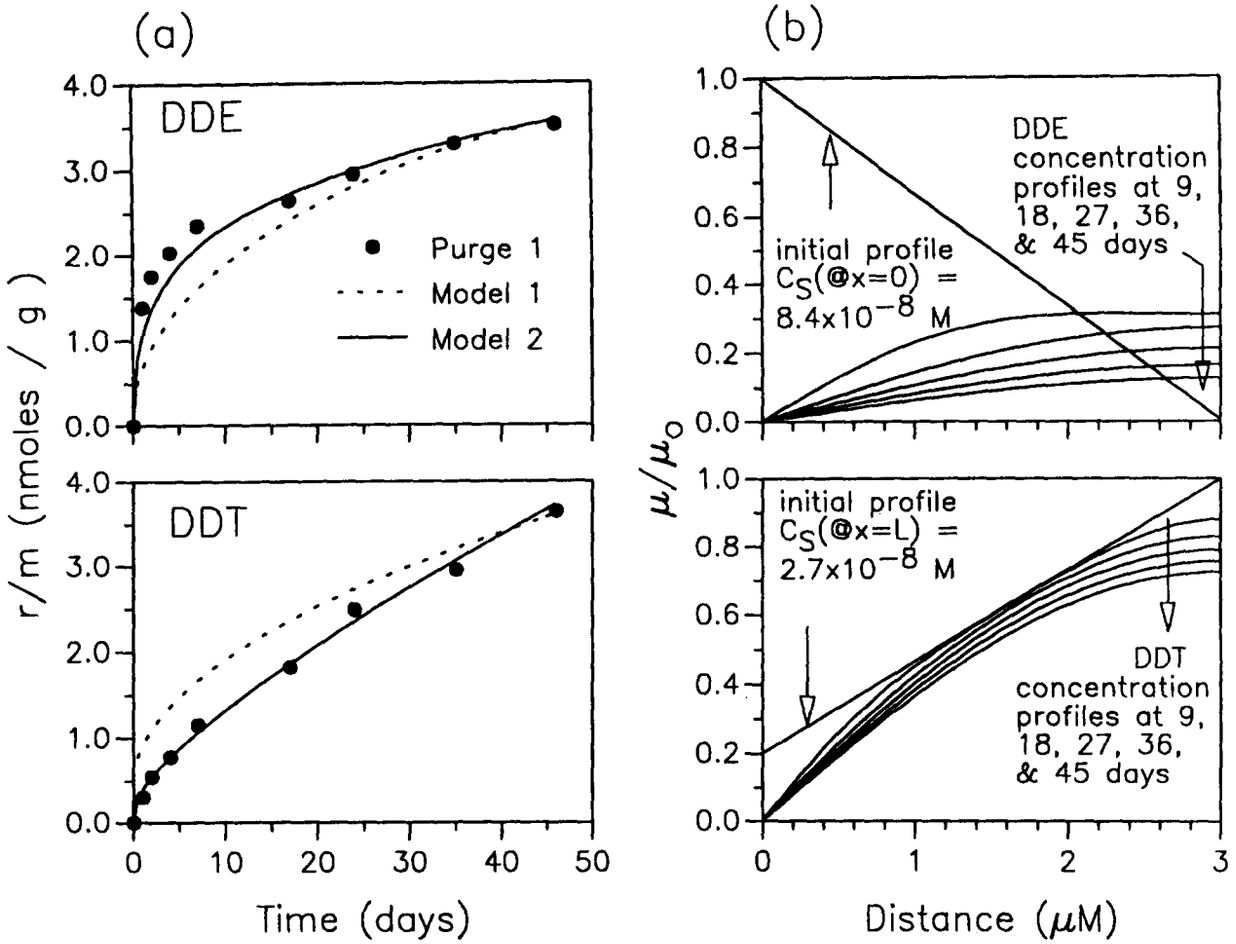

FIG. 6. (a) Purge 1 Data and Simulations Using Uniform Initial Concentration of Fig. 5 (Model 1); (b) Initial Profiles (Model 2); For Model 2, D = 2 × 10^{-14} and 1.2 × 10^{-14} cm²/s for DDT and DDE, Respectively

that for DDT. If decay occurs abiotically or biotically within a different sediment phase than the sorptive phase, different concentration profiles may be expected in the sorptive phase, as reaction (or wash out) would prevent the attainment of equilibrium. DDT at the surface may desorb, be transformed to DDD or DDE, which in turn may readsorb. If reaction and mass transfer, in situ, are on the same order of magnitude, this process would deplete the exterior DDT concentration and produce higher surface concentrations of DDD and DDE. We may test model sensitivity to gradients by varying the initial concentration profiles within the sediment. Fig. 6(a) compares DDT and DDE data from purge one to simulations using the linear concentration profiles, at $t = 0$, indicated on Fig. 6(b). For DDE, although a more precise fit is achieved by adjustment of D by 25%, the initial profile is very unreasonable as diffusion occurs rapidly and in both directions over the time scale of the experiment. Alternatively, a comparable fit easily could be achieved with a "multislab model" by varying volumes and diffusional distances of several slabs. For DDT, the initial profile is more reasonable as subsequent profiles are lower and virtually parallel. In this case, D required substantial adjustment from 7×10^{-16} cm²/s (uniform initial profile) to 2×10^{-14} cm²/s^{-1}, resulting in what may be considered a minor improvement in the calculated removal.

The magnitude of the diffusion coefficient, D, defines the relative resistance to mass transfer through the matrix. For similar compounds, the diffusion coefficient is a function of molecular size, which generally correlates to molecular surface area and molecular weight. The molecular weight of DDT (354.49) is higher than DDD (320.05), which in turn is similar to that of DDE (318.05). The relative release rates may be expected; however, the absolute differences based on uniform concentration profiles (i.e., factor of 21) is high. This discrepancy disappears, however, if a positive inward concentration gradient for DDT is assumed, as the value of D is very sensitive to this type of gradient.

As a final analysis, we examined whether this initial DDT profile was reasonable based upon the extended time frame of contamination. Because nothing is known regarding the mass transfer history of DDT in this particular sediment mass, the simplest yet worst case scenario was assumed for purposes of discussion. The assumptions are (1) At $t = 0$, particles are nearly saturated with DDT at 290 nmol/g (this conentration is based on the water solubility of DDT); (2) $D = 7 \times 10^{-16}$ cm²/s; and (3) mass transfer through advection of or diffusion through the aqueous phase limits loss from the system such that the concentration at year 25 is approximately the same as that occurring in the sediment today. This loss may be controlled by adjusting k_g that simply controls first-order decay from the system. Results of this simulation are shown in Fig. 7 with the sediment mass to volume ratio set to one. For this simulation, k_g was adjusted to 9.5×10^{-5} s^{-1} (halflife of 2.9 h). Under these conditions, loss from the system is controlled largely by this term, yet a moderate concentration gradient is predicted in the sediment at year 25.

Gradients may form and stay formed by other mechanisms neglected in this simple scenario. Over time, particles are dynamic due to chemical, biological, and physical diagenetic processes. These processes may result in continuous variation in diffusive path lengths and diffusive directions (i.e., geom-

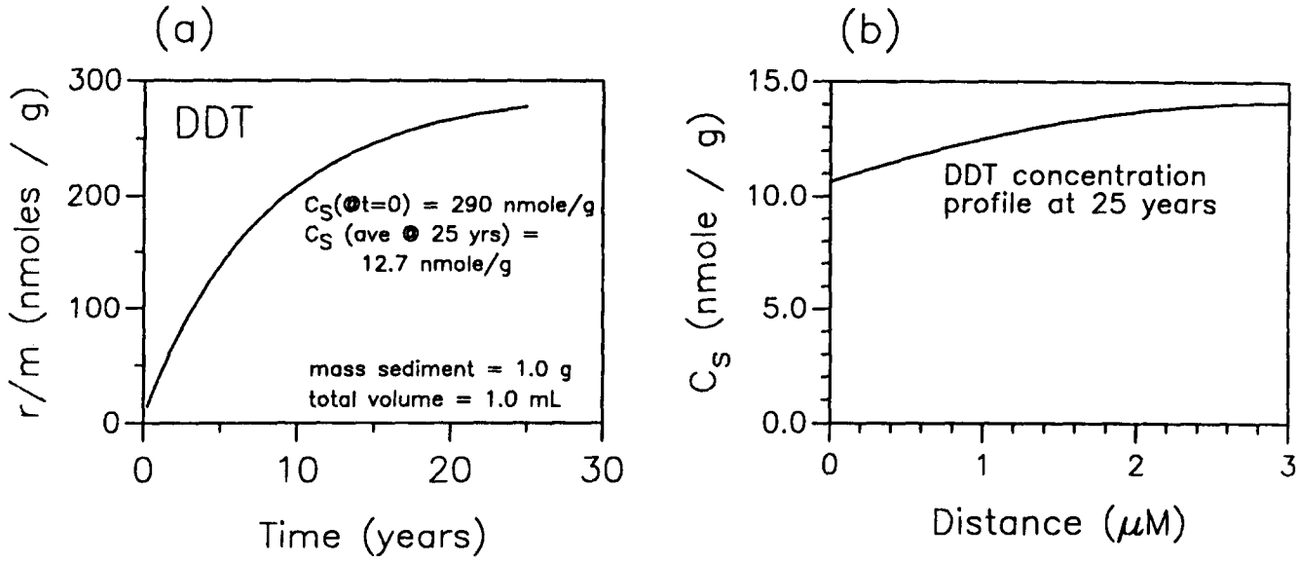

FIG. 7. Simulations of DDT Release from a 1 g/mL Sediment Solution with $k_g = 10^{-5}$ s^{-1} and 290 nmole/g Initial Homogeneous DDT Concentration

etries). Diffusional paths may become obstructed by mineral layers, increasing resistance to removal and leading to true sorption hysteresis.

An alternate interpretation was recently suggested by Carroll et al. (1994), who examined desorption of PCBs from Hudson River sediments. They proposed that sorption to swollen and condensed humic material may account for rapid and very slow mass transport, respectively. The hypothesis that some humic material is "condensed," similar to synthetic glassy polymers, suggests diffusion within this matrix may be a function of solute concentration and time, that is, non-Fickian. The indeterminate chemical and physical nature of humic material makes this hypothesis difficult to prove.

CONCLUSIONS

Gas-purge induced desorption for 46 days of the Indian Creek sediment resulted in 22, 58, and 75% average removal for DDT, DDD, and DDE, respectively. The time to reach 25% removal was approximately 50 days for DDT and 4 days for DDD. Purge experiments were performed at an air flow rate of 1 L/min at sediment concentrations ranging from 0.37 to 3.7 g/200 mL with no notable difference in removal (nmol/g sediment) over this range for DDT and for DDE.

Results were compared to simulations of a simple Fickian diffusion model in which diffusion is assumed to occur in one direction from a fixed depth to a plane surface. The concentration at this surface is assumed to be in equilibrium with the aqueous concentration, which in turn is depleted through first-order decay to the gas phase. Simulations and experimental data indicate that the loss of DDD across the liquid-gas interface is somewhat limiting at high sediment concentrations.

Simulations also indicate that DDT is more resistant to removal at short time periods compared to either DDD or DDE. This suggests that differences may occur in the initial concentration profiles of the three compounds within the sediment particles. Both the gradual loss of chemical from the sediment (i.e., washout) and short-term sediment diagenesis may play roles in the formation of these gradients.

Finally, this work has some general implications for the engineering community regarding soil/sediment remediation methods and site assessment. First, while it is generally accepted that desorption often is a rate-limiting factor for pump-and-treat, gas stripping, and most biological processes, the magnitude of this effect is often not realized. All of these methods presumably require transfer of the contaminants to or through the aqueous phase. The methods used in this study define the absolute maximum removal rate through this pathway (i.e., aqueous phase depletion). We show that for DDT, even with an aqueous phase half-life of 2.9 h, decades are required to deplete the sediment phase, if the sediment phase is unreactive. Clearly, this is the motivation behind studies that attempt to facilitate removal through the addition of cosolvents, surfactants, or colloids. Second, the initial concentration gradient within individual particles is an important site-specific parameter that is often ignored. This may be the reason why several reported diffusion coefficients for PCBs and other compounds, measured using historically contaminated sediments, are orders of magnitude lower than estimated values. Existing gradients can only be assessed experimentally. How sediment diagenesis effects or contributes to these gradients is largely unknown.

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APPENDIX II. NOTATION

The following symbols are used in this paper:

A = slab cross sectional area (cm^2);
C_{aq} = concentration in liquid phase (mol/mL);
C_g = bulk gas phase conentration (mol/mL);
C_o = initial concentration (mol/kg);
C_s = solute concentration in soil (mol/kg);
C_t = total concentration at time t (mol/L);
D = diffusion coefficient (cm^2/s);
DDD, p,p'-DDD = 2,2-Bis(4-chlorophenyl)-1,1-dichloroethane;
DDE, p,p'-DDE = 2,2-Bis(4-chlorophenyl)-1,1-dichloroethylene;
DDT, p,p'-DDT = 1,1-Bis(4-chlorophenyl)-2,2,2-trichloroethane;
f_t = fraction of total mass released at time t, dimensionless;
f_{oc} = fraction soil organic carbon (dimensionless);
k = diffusive transport coefficient ($s^{-0.5}$);
k_g = mass transfer coefficient (s^{-1});
K_{oc} = partition coefficient to soil organic carbon (L/kg);
K_{ow} = octanol-water partition coefficient, dimensionless;
K_{wall} = wall-water partition coefficient, dimensionless;
L = diffusive path length (cm);
m = Henry's Law constant, (mol/mL air)/(mol/mL water);
M_t = total mass that has left the source at time t (mol);
M_∞ = total mass of solute in soil, mol;
r/m = cumulative chemical mass released per mass dry weight sediment (mol/g);
t = time (s);
V_L = liquid volume (mL);
x = distance (cm);
μ = slab concentration (mol/cm^3) organic matter;
μ_o = initial concentration (mol/cm^3) organic matter; and
ρ_h = density of soil organic carbon (g/cm^3).

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