

Mathematical Modeling of Controlled-Release Kinetics of Herbicides in a Dynamic-Water-Bath System

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Abstract

Release of herbicides from lignin-based formulations follows a diffusion-controlled mechanism. For mathematical modeling of diffusive transport, the conventional approach is to assume sink conditions at both surfaces of polymeric matrix. This boundary condition proved to be inadequate to describe experimental data obtained in a water dynamic bath system. However, satisfactory descriptions for this system were obtained when a stagnant unstirred layer of herbicide solution was used as the boundary condition. The adequacy of the model incorporating this new boundary condition was statistically tested using the Fisher test at a confidence level of 95% and plotting the residual distribution.

Index Entries: Mathematical modeling; controlled release; herbicides; lignin; anetryn; diuron; diffusion.

Introduction

Lignin is a byproduct of several industrial processes, mainly pulping and production of fermentable sugars from biomass. The use of lignin as matrix for controlled-release systems with a large number of pesticides has been extensively studied (1) and can be synergistic with chemical production from cellulose.

The release kinetics of herbicides (active ingredient [AI]) from lignin matrices is a very important aspect to be investigated in order to predict

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both dosage of AI used at the time and the AI destination when applied in acceptor systems containing an aqueous phase such as the soil.

Release kinetics studies usually are carried out by monitoring the amount of herbicide released into a static or dynamic water bath (2–4). In the static water bath system (SWBS), the controlled-release formulations (CRFs) are immersed in deionized water contained in flasks. In this system, the sampling is performed by changing all the water of the flasks in a defined time interval. On the other hand, in the dynamic water bath system (DWBS), the CRFs are placed in cylindrical tubes of glass, with sintered discs in the top and bottom of the columns for retention of the particles. Water is continuously pumped into the column. Samples of the effluent of the column are periodically collected in order to determine herbicide concentration (4).

In previous studies, a mathematical model was developed for the release kinetics based on a diffusive transport mechanism described by the second Fick's law (5,6). In this model, sink conditions were adopted: the concentrations of AI in both slab surfaces are assumed to be zero during the entire time range of herbicide release. In a preliminary analysis, the model incorporating this boundary condition proved to be valid to describe the release kinetic data obtained in the SWBS. However for the DWBS, this approach was not able to describe the kinetic data satisfactorily. This result is dubious because the concentration in the slab surface in the DWBS is much lower than in the SWBS. A hypothesis to explain this fact might be that the static system is all unstirred and thus more susceptible to being modeled as a single process. To avoid the lack of fit of the model to the experimental data in the DWBS, another boundary condition at the slab surface is used. This new boundary condition incorporates the existence of a stagnant unstirred layer at the interface between the slab surface and the release medium.

Materials and Methods

The CRFs employed in release experiments in the DWBS were manufactured using lignin extracted from sugarcane bagasse pretreated by the steam explosion process in a pilot plant in our laboratory. Lignin was recovered by precipitation with HCl and characterized as described by Ferraz et al. (3). The lignin and herbicide were melted in equal amounts in stainless-steel concave recipients and immersed in a silicon bath with temperatures between 170 and 200°C, and the mixture was homogenized. After complete homogenization, the recipients were cooled at room temperature. The formulations were ground and sieved to select a range of granule size from 0.71 to 1.00 mm. Two types of CRFs were prepared: CRFD (with diuron: 3-[3,4-dichlorophenyl]-1,1-dimethylurea; 94.8% purity) and CRFA (with ametryn: 2-ethylamino-4-isopropylamino-6-methylthio-1,3,5-triazine; 97.8% purity) (4).

Release Experiments in a DWBS

In the DWBS the CRF samples were weighed and allocated in glass columns 40 mm long and 18 mm in diameter that contained sintered disks in the top and bottom for retention of the particles. The system was maintained at 30°C and fed on the bottom with deionized water at a flow rate of 2 mL/min. The effluent was collected on the top and stored in glass flasks that were changed periodically. The herbicide concentration in the flasks was determined by high-performance liquid chromatography using a 1.8×200 mm C-18 column (HP-RP18). Diuron was eluted with a methanol/water solution (7:3 [v/v]) at 0.7 mL/min and detected at 280 nm. Ametryn was eluted with a methanol/sodium phosphate buffer (pH 5.0) solution (7:3 [v/v]) at 0.8 mL/min and detected at 250 nm (4).

Modeling of Release Kinetics

The release rate of AI is controlled by a diffusion mechanism, mathematically described by the second Fick's law (5–7). According to this law, the spatial and temporal profiles of AI concentration are governed by Eq. 1:

$$\frac{\partial c_p}{\partial t} = D_{eff} \frac{\partial^2 c_p}{\partial x^2} \quad (1)$$

in which c_p is the AI concentration in the pores (g/cm), D_{eff} is the effective diffusion coefficient (cm²/d), x is the spatial coordinate (cm), and t is the time (d) (7).

To solve Eq. 1, it is necessary to formulate the initial and boundary conditions. The initial condition is given by

$$c_p(x, t = 0) = \frac{M_0}{\epsilon AL} \quad (2)$$

in which M_0 is the initial amount of the content of AI in the slab (g), ϵ is the matrix porosity, A is the slab area (cm²), and L is the matrix thickness (cm) (4).

In the present study, two types of boundary conditions were used at the slab surface: sink conditions and stagnant unstirred layer.

Model Incorporating Sink Conditions at Slab Surface

The sink conditions at both slab surfaces are described by Eq. 3:

$$c_p(0, t) = c_p(L, t) = 0 \quad (3)$$

By solving Eq. 1 using initial and boundary conditions (Eqs. 2 and 3), Eq. 4 is obtained:

$$c_p(x, t) = \frac{4M_0}{\epsilon AL\pi} \sum_{n=0}^{\infty} \left\{ \frac{1}{2n+1} \exp \left[-\frac{(2n+1)^2 \pi^2 D_{eff}}{L^2} t \right] \sin \left[\frac{(2n+1)\pi x}{L} \right] \right\} \quad (4)$$

From Eq. 4, Eq. 5, describing the cumulative amount of AI released at time t (M_t), can be developed (5,7):

$$\frac{M_t}{M_0} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \left(\frac{\exp \left[-\frac{(2n+1)^2 \pi^2 D_{eff} t}{L^2} \right]}{(2n+1)^2} \right) \quad (5)$$

Since granule size was the same for all CRFs used in the release experiments, the value of slab thickness L can be assumed constant and the D_{eff} parameter can be replaced by D^* (d^{-1}), which incorporates the following constants (5):

$$D^* = \frac{\pi^2 D_{eff}}{L^2} \quad (6)$$

Model Incorporating a Stagnant Unstirred Layer as Boundary Condition at Slab Surface

The mass transfer of herbicide through a stagnant unstirred layer at both slab surfaces is described by Eq. 7:

$$-D_{eff} \frac{\partial c_p}{\partial x} = k(c_p^* - c_b) \quad (7)$$

in which c_p^* is the concentration in the bulk fluid (g/cm), c_b is the concentration in the surrounding medium (g/cm), and k is the parameter of mass transfer by convection (cm/d).

If the slab $0 < x < L$ is initially at uniform concentration c_0 and if the law of mass transfer at both surfaces follows Eq. 7, the solution of Eq. 1 is:

$$\frac{c_p - c_0}{c_p^* - c_0} = 1 - \sum_{n=0}^{\infty} \frac{2Bi \cos(\beta_n x/2L) \exp(-\beta_n^2 D_{eff} t/4L^2)}{(\beta_n^2 + Bi^2 + Bi) \cos \beta_n} \quad (8)$$

in which β_n are the positive roots of the equation:

$$\beta \tan \beta = Bi \quad (9)$$

in which

$$Bi = Lk/D_{eff} \text{ (Biot number)} \quad (10)$$

The six first roots of Eq. 9 are listed in Table 1 (8).

Table 1
Six First Roots of $\beta \tan \beta = Bi$

Bi	β_0	β_1	β_2	β_3	β_4	β_5
0	0	3.1416	6.2832	9.4248	12.5664	15.7080
0.01	0.0998	3.1448	6.2848	9.4258	12.5672	15.7086
0.1	0.3111	3.1731	6.2991	9.4354	12.5743	15.7143
0.2	0.4328	3.2039	6.3148	9.4459	12.5823	15.7207
0.5	0.6533	3.2923	6.3616	9.4775	12.6060	15.7397
1.0	0.8603	3.4256	6.4373	9.5293	12.6453	15.7713
2.0	1.0769	3.6436	6.5783	9.6296	12.7223	15.8336
5.0	1.3138	4.0336	6.9096	9.8928	12.9352	16.0107
10.0	1.4289	4.3058	7.2281	10.2003	13.2142	16.2594
100.0	1.5552	4.6658	7.7764	10.8871	13.9981	17.1093
∞	1.5708	4.7124	7.8540	10.9956	14.1372	17.2788

For this approach, the cumulative amount of AI released at time t (M_t) is given by (7):

$$\frac{M_t}{M_0} = 1 - \sum_{n=0}^{\infty} \frac{2Bi^2 \exp(-4\beta_n^2 D^* t / \pi^2)}{\beta_n^2 (\beta_n^2 + Bi^2 + Bi)} \quad (11)$$

An asymptotic analysis of the meaning of the boundary condition represented by Eq. 7 indicates that for high values of k (convective parameter), the thickness of stagnant unstirred layer is decreased and c_0 tends to c_p . In a limit case, when k tends to an infinite value, Bi also tends to an infinite value. By analyzing Eq. 11 when $Bi \rightarrow \infty$, one obtains

$$\lim_{Bi \rightarrow \infty} \frac{M_t}{M_0} = \lim_{Bi \rightarrow \infty} \left[1 - \sum_{n=1}^{\infty} \frac{2Bi^2 \exp(-4\beta_n^2 D^* t / \pi^2)}{\beta_n^2 (\beta_n^2 + Bi^2 + Bi)} \right] = 1 - \frac{\infty}{\infty} \quad (12)$$

The ∞/∞ indetermination in Eq. 12 can be avoided by using L'Hôpital's rule. The final result of this mathematical procedure is

$$\lim_{Bi \rightarrow \infty} \frac{M_t}{M_0} = 1 - \sum_{n=1}^{\infty} \frac{2 \exp(-4\beta_n^2 D^* t / \pi^2)}{\beta_n^2} \quad (13)$$

When $Bi \rightarrow \infty$, it can be demonstrated that

$$\beta_n = \frac{\pi}{2} (2n + 1) \quad (14)$$

By substituting Eq. 14 in Eq. 13, Eq. 5 is obtained again. This result indicates that for high Bi values, the external resistance to mass transfer can be neglected and Eq. 11 is equivalent to Eq. 5.

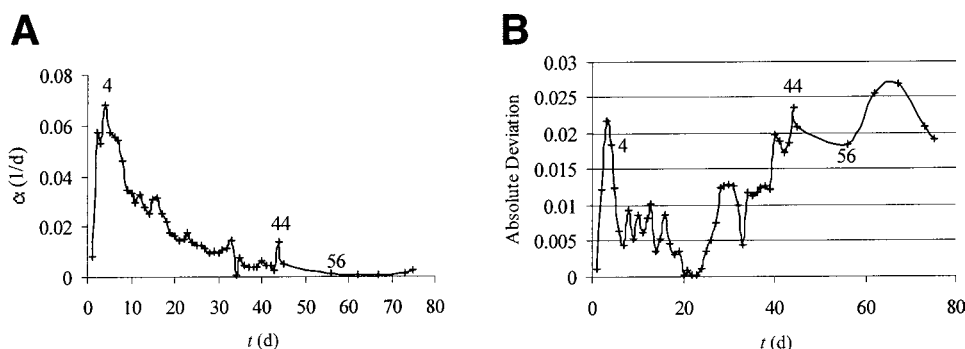


Fig. 1. Graphics used during the elimination procedure of experimental data: (A) average rate of herbicide cumulative amount released and (B) absolute deviation.

Results and Discussion

Prior to the mathematical modeling, an analysis of the experimental data was carried out aiming to remove the inadequate experimental data as well as to delimit the time range for which Eqs. 5 and 11 are valid.

Exclusion of Inadequate Experimental Data

The utilization of the original experimental data set resulted in a significant lack of fit of the model for both boundary conditions used at the slab surface. Consequently, the experimental data without an expected behavior were removed from the original experimental data set, according to the following graphic procedure: Figure 1A shows the behavior of the ratio $\alpha = [(M_t/M_0)_i - (M_t/M_0)_{i-1}] / (t_i - t_{i-1})$ as a function of the time t_i (in which $i = 1, 2, 3, \dots, n$ and n is the number of experimental data). The ratio α can be interpreted as an average rate of the cumulative amount of herbicide released in the time interval between t_i and $t_i - 1$. Figure 1B shows the absolute value of the difference between two data of $(M_t/M_0)_i$ obtained in replicated experiments as a function of the time t_i . The absolute value of difference provides a rough estimate of the experimental error.

Figure 1A,B clearly indicates that some experimental data must be removed from the original set. Figure 1A shows the existence of an initial period (0–4 d) during which the average rate increases and decreases oscillating at the time. Taking into account that during the diffusive process the release rate decays asymptotically at the time, the oscillations observed in the initial period may be attributed to the occurrence of two phenomena: slab entumesciment and dissolution of herbicide initially existing on the slab surface. Thus, the experimental data concerning the initial period were discharged. Experimental datum obtained on d 44 is seen as a peak in Fig. 1A and is inaccurate according to Fig. 1B (high value of deviation). For these reasons, this experimental datum was also excluded. After 56 d, the release rate is very close to zero, resulting in inaccurate determinations of herbicide concentration in the medium. This fact explains the high values

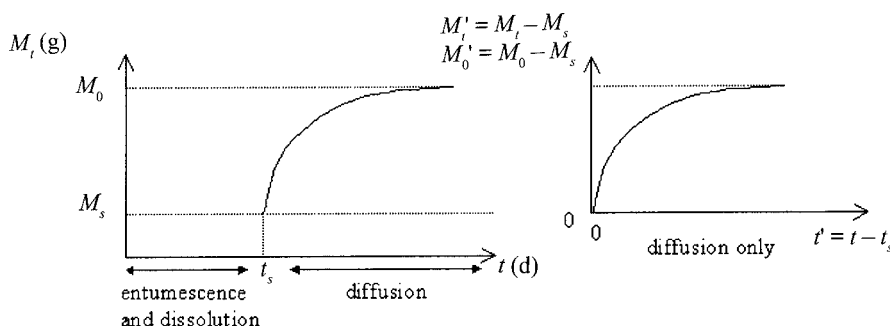


Fig. 2. Schematic representation of change in variables.

of deviation in Fig. 1B for times above 56 d. The data obtained in this experimental region were not used in the mathematical modeling.

Delimitation of Time Range

During Which Diffusive Models Are Valid

Equations 5 and 11 describe only the diffusion of herbicide from slab to acceptor medium. However, other phenomena occur during the first days of the release experiment: the slab entumescence and dissolution of herbicide initially existing on the slab surface. Because the diffusive models take into account that in the start of release ($t = 0$), $M_t/M_0 = 0$, it is necessary to write Eqs. 5 and 11 in terms of the corrected variables t' and M'_t , in order to describe exclusively the diffusive phenomenon as shown schematically in Fig. 2.

To correct the time variable, it is necessary to realize the following subtraction:

$$t' = t - t_s \quad (15)$$

in which t' is time data corrected and t_s is the initial time during which the entumescence and dissolution phenomena occur.

Correction of the cumulative mass released may be realized according to the following relationship:

$$\frac{M'_t}{M'_0} = \frac{M_t - M_s}{M_0 - M_s} \quad (16)$$

in terms of cumulative amount

$$\frac{M'_t}{M'_0} = \frac{M_t/M_0 - M_s/M_0}{1 - M_s/M_0} \quad (17)$$

in which M'_t/M'_0 is the corrected cumulative amount of herbicide released and M_s/M_0 is the cumulative mass released by dissolution.

Table 2
Values of Parameters M_s and t_s
Used for Correction of Release Curves

CRFs	M_s/M_0	t_s (d)
CRFD	0.074	6
CRFA	0.195	4

Table 3
Diffusion Coefficients Estimated
for FLCs of Diuron and Ametryn
Considering Sink Conditions
on Slab Surface (Eq. 5)

CRFs	D^* (d ⁻¹)
CRFD	0.0067 ± 0.0003
CRFA	0.055 ± 0.001

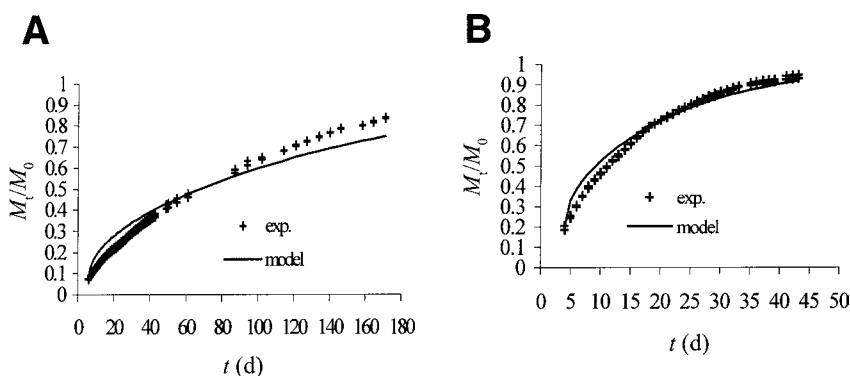


Fig. 3. Plot of experimental and calculated values for the model incorporating sink conditions at slab surface: (A) CRFD; (B) CRFA.

The M_s/M_0 and t_s values for the replicated experiments were estimated by inspection of similar plots shown in Fig. 1A. These values are presented in Table 2.

Mathematical Modeling Incorporating Sink Conditions at Slab Surface

The values of the diffusion coefficient (D^*) estimated by nonlinear regression (9) are presented in Table 3 for the two CRFs used, and a plotting of experimental data and model predictions is shown in Fig. 3. Figure 3 shows that there was a clear lack of fit of the model to the experimental data for both CRFs used. To quantify statistically this lack of fit, the tables of analysis of variance (ANOVA) were built for the two herbicide formula-

Table 4
ANOVA for Fit of Eq. 5 to Corrected Experimental Data Obtained with CRFD

Source	Sum of squares	Degrees of freedom	Mean square	F ratio	F _{95%} (tabulated)
Regression	3.554	1	3.554	1204	3.932
Residues	0.307	104	0.0030		
Lack of fit	0.304	51	0.0060	132	1.583
Pure error	0.0024	53	0.000045		
Total	3.861	105			
R ²	0.9205				
R ² maximum	0.9995				

Table 5
ANOVA for Fit of Eq. 5 to Corrected Experimental Data Obtained with CRFA

Source	Sum of squares	Degrees of freedom	Mean square	F ratio	F _{95%} (tabulated)
Regression	3.024	1	3.024	2422	3.974
Residues	0.090	72	0.0012		
Lack of fit	0.087	35	0.0025	28	1.739
Pure error	0.0032	37	0.000088		
Total	3.114	73			
R ²	0.9711				
R ² maximum	0.9992				

Table 6
Parameter Estimates for Model Incorporating
a Stagnant Unstirred Layer
as Boundary Condition at Slab Surface (Eq. 11)

CRF	D* (d ⁻¹)	Bi
CRFD	0.0209 ± 0.0001	2.0 ± 0.1
CRFA	0.118 ± 0.005	2.8 ± 0.2

tions (Tables 4 and 5). For both CRFs, the F ratio value calculated was greater than the corresponding tabulated value. This analysis, however, does not show the nature of this inadequacy, which is attributed here to the use of an inappropriate boundary condition at the slab surface.

Mathematical Modeling Incorporating a Stagnant Unstirred Layer as Boundary Condition at Slab Surface

The parameter estimation results for the model incorporating a stagnant layer as boundary condition on the slab surface are presented in Table 6

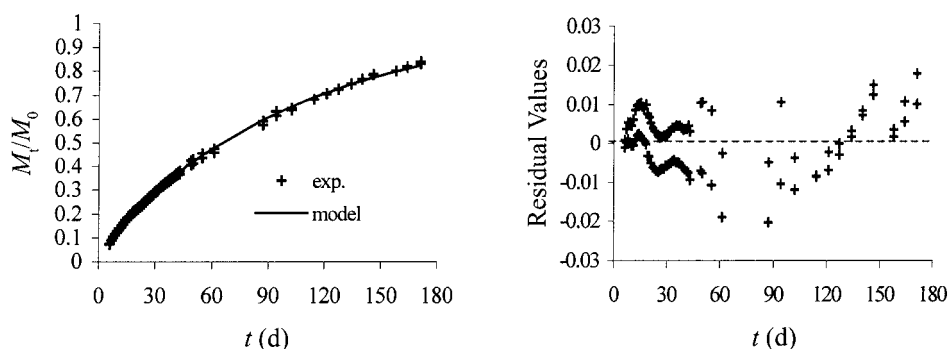
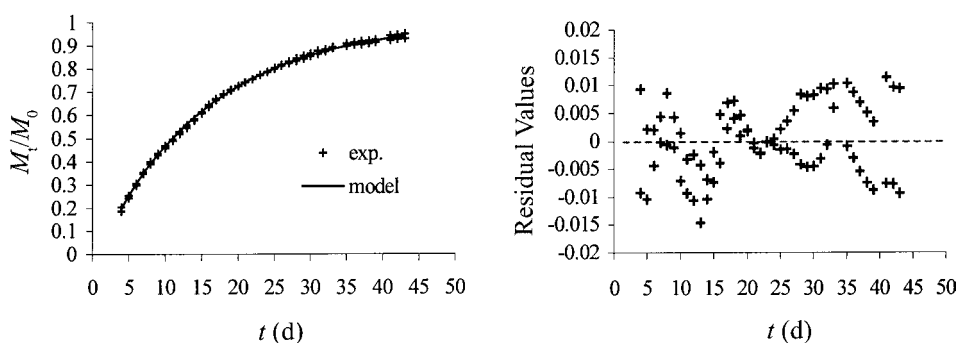
A**B**

Fig. 4. Plot of experimental and calculated values for the model incorporating a stagnant unstirred layer as boundary condition: **(A)** CRFD; **(B)** CRFA.

for both CRFs used. A plot of the experimental data and model predictions and the distribution of the residual values are shown in Fig. 4. A good fit of the model to the experimental data may be observed for both CRFs. Moreover, the residuals distribution is randomized in both cases. To confirm the adequacy of the model, ANOVA is presented in Tables 7 and 8 for each herbicide formulation employed. For both CRFs investigated, the high values of F ratio for regression and the small values of F ratio for lack of fit indicate that the model incorporating a stagnant unstirred layer as the boundary condition at both slab surfaces is adequate to describe the experimental data obtained in the DWBS.

Relevant information obtained from the analysis of data presented in Tables 3 and 6 is that the value of D^* estimated using a stagnant unstirred layer at the slab surface is higher than the ones estimated using the sink conditions. This can explain some of our experimental data on release in soil, which show that the release rate is faster in comparison with that observed in the SWBS and DWBS. This result suggests that the stagnant unstirred layer in the slab surface is reduced in the soil system, probably

Table 7
ANOVA for Fit of Eq. 11 to Experimental Data Obtained with CRFD

Source	Sum of squares	Degrees of freedom	Mean square	F ratio	F _{95%} (tabulated)
Regression	5.623	1	5.523	109435	3.932
Residues	0.0053	104	0.000051		
Lack of fit	0.0029	51	0.000058	1.317	1.583
Pure error	0.0024	53	0.000045		
Total	5.629	105			
R ²	0.9991				
R ² maximum	0.9996				

Table 8
ANOVA for Fit of Eq. 5 to Experimental Data Obtained with CRFA

Source	Sum of squares	Degrees of freedom	Mean square	F ratio	F _{95%} (tabulated)
Regression	4.0922	1	4.0923	5.5396	3.974
Residues	0.0053	72	0.000074		
Lack of fit	0.0021	35	0.000059	0.678	1.739
Pure error	0.0032	37	0.000087		
Total	4.0976	73			
R ²	0.9987				
R ² maximum	0.9992				

owing to an adsorption mechanism of herbicide in the soil. To obtain secure conclusions, new experiments must be conducted to understand this phenomenon.

Conclusion

The utilization of a boundary condition incorporating a stagnant unstirred layer of herbicide solution at both slab surfaces provided a good description of release kinetics in the DWBS. The model considering sink conditions at the slab surface is a simplification that is not valid for describing release kinetics data obtained in the DWBS. The results obtained in this study are an advancement in the search of a relationship coupling the controlled release kinetic data obtained in a simple system (water bath) with those obtained in a complex system (soil). However, the practical contribution of the model incorporating a stagnant unstirred layer as the boundary condition at both slab surfaces depends on the extent to which the model allows one to obtain, from laboratory studies, fundamental values of diffusion coefficients that can be extrapolated from the laboratory to the field.

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