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Numerical simulation of transport and transformation of insecticide 1-(2-chlorobenzoyl)-3-(4-chlorophenyl) urea in unsaturated soil*

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Abstract A numerical simulation model of pesticide transport and transformation in unsaturated soil is presented in this paper. The model was developed under basic principles of movement of water and solute in soil under transient condition and overall consideration water flow: pesticide convection, diffusion, dispersion, sorption and degradation. The model was tested for the persistence and leaching of 1-(2-chlorobenzoyl)-3-(4-chlorophenyl) urea (CCU) using data from soil columns under laboratory conditions. The results of the test indicate that the modeling approach is simple and effective in describing movement and transformation of pesticides in soils.

Keywords: numerical simulation; insecticide; transport; transformation; soil.

INTRODUCTION

The fate of pesticides in environment involves a series of processes, many of which occur in the unsaturated zone of soil. The main processes relating to translocation and transformation of pesticides in soil include: 1. run off from surface soil, 2. convection, diffusion and dispersion in soil water, 3. sorption and degradation in soil, 4. uptake by plants, and 5. volatilization. In the past decade, numerical simulation approach was widely used to study the transport and transformation of pesticides in soil for its convenience and effectiveness (Carsel, 1985; Wagenet, 1986). In this research, a simulation model developed for predicting the fate of pesticides in unsaturated soil and results of validation of the model for the transport and transformation of CCU in soil are presented.

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MATHEMATICAL DESCRIPTION OF THE PROBLEM

The transport of a pesticide lies mainly in the movement of the chemical as a solute in soil water. Therefore the model that describes the transport and transformation of a pesticide in unsaturated soil consists of soil water flow submodel and pesticide movement submodel (Nielsen, 1986; Lei, 1988).

Soil water flow submodel

The equation of vertical flow of soil water can be deduced by the Darcy's law and continuity equation. The basic equation can be written by

$$\frac{\partial\theta}{\partial t}=\frac{\partial}{\partial Z}\left[D(\theta)\frac{\partial\theta}{\partial Z}\right]-\frac{\partial K(\theta)}{\partial Z} \tag{1}$$

where, θ is the volumetric water content of the soil (cm^3/cm^3); $D(\theta)$ is water diffusion coefficient in unsaturated soil (cm^2/min); $K(\theta)$ is water conductivity of unsaturated soil (cm/min): Z is depth of soil from the surface (cm); t is time (min).

Generally, $D(\theta)$ and $K(\theta)$ can be expressed by the following equations:

$$D(\theta)=D_o\,\theta^m\,; \tag{2}$$

$$K(\theta)=K_o e^{\beta\theta}\,, \tag{3}$$

where D_o, m, K_o and β are coefficients.

The initial and boundary conditions can be written as:

$$\begin{cases} \theta=\theta_i & t=0,\ Z\geqslant 0, \\ -D(\theta)\partial\theta/\partial Z+K(\theta)=R & t>0,\ Z\geqslant 0, \\ \theta=\theta_i & t>0,\ Z=L, \end{cases} \tag{4}$$

where, θ_i is initial water content of soil (cm^3/cm^3); R is rate of rainfall (cm/min) and L is depth of soil (cm).

Pesticide movement submodel

According to hydrodynamic dispersion theory, one-dimensional diffusion-convection equation for the movement of a pesticide in unsaturated soil can be written as:

$$\frac{\partial(\theta C)}{\partial t}+\frac{\partial(\rho C_s)}{\partial t}=\frac{\partial}{\partial Z}\left[D_{sh}(\theta,q)\frac{\partial C}{\partial Z}\right]-\frac{\partial(qC)}{\partial Z}\pm\Phi, \tag{5}$$

where, C is concentration of the pesticide in soil solution ($\mu g/cm^3$): C_s is concentration of pesticide adsorbed to the soil phase ($\mu g/g$); ρ is soil bulk density (g/cm^3); q is soil water flux density (cm/min); D_{sh} (θ,q) is hydrodynamic dispersion coefficient (cm^2/min); Φ is source or sink of the pesticide ($\mu g \cdot cm^{-1}.min^{-1}$) such as degradation.

In most cases, when concentration of the pesticide is very low, the reaction process of sorption and desorption of the pesticide can be regarded as an instantaneous equilibrium process. and described by a simple linear equation:

$$C_s = K_d C, \tag{6}$$

where, K_d is adsorption constant of the pesticide (g/cm^3).

Degradation of a pesticide in soil can be described by a pseudo first-order reaction as:

$$dC_T / dt = -K C_T, \tag{7}$$

where, C_T is concentration of the pesticide in soil and K is the rate constant of degradation (1/min).

The source or sink term can be written by

$$\Phi = -K(\theta + \rho K_D) C. \tag{8}$$

The initial and boundary conditions of the model can be expressed by the flowing equations:

$$\begin{cases} C = C_o(Z) & t=0,\ Z \geqslant 0, \\ -D_{sh}(\theta, q)\partial C/\partial Z + qC + 0 & t \geqslant 0,\ Z=0, \\ C = C_o(1) & t \geqslant 0,\ Z=\mathrm{L}. \end{cases} \tag{9}$$

NUMERICAL SOLUTION OF THE MODEL

In most cases, because of the complexity of the problem, there is no analytical solution for the model. The finite difference discrete numerical approach is employed here to solve the equations of the model for the movement of pesticides in unsaturated soil.

Numerical solution of water flow submodel

The discrete network of the calculation region is shown in Fig. 1.

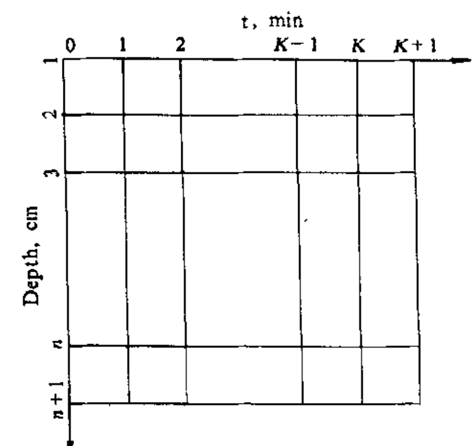

Fig. 1 Discrete network of a continuous 1-D region

The implicit finite differential Equation (1) is given by

$$\frac{\theta_i^{k+1} - \theta_i^k}{\Delta t} = \frac{D_{i+\frac{1}{2}}^{k+1}\left(\theta_{i+1}^{k+1} - \theta_i^{k+1}\right) - D_{i-\frac{1}{2}}^{k+1}\left(\theta_i^{k+1} - \theta_{i-1}^{k+1}\right)}{\Delta Z^2} - \frac{K_{i+1}^{k+1} - K_{i-1}^{k+1}}{2\Delta Z} \tag{10}$$

where, i, k are numbers of depth and time nets; Δt is time increment (min); Z is depth increment (cm).

The finite differential equation of the boundary condition can be written by means of water equilibrium in half net near the surface.

Numerical solution of pesticide movement submodel

The control volume method is employed to solve the diffusion-convection equation. The discrete network is the same as that in water flow submodel. Boundary is set up in the middle of two grid points (Fig.2a). Equation (8) may also be written as follows:

$$\frac{\partial}{\partial t}(\hat{\rho}C)+\frac{\partial J}{\partial Z}=SC, \tag{11}$$

in which,

$$\hat{\rho}=\theta+\rho K_D,$$

$$J=qC-D_{sh}(\theta,q)\frac{\partial C}{\partial Z},$$

$$S=-K(\theta+\rho K_D).$$

Integration of Equation (11) over control volume (Fig.2b) is given by

$$\int_{Z_{i-\frac{1}{2}}}^{Z_{i+\frac{1}{2}}}\int_{tk}^{tk+1}\frac{\partial}{\partial t}(\hat{\rho}C)dtdZ+\int_{tk}^{tk+1}\int_{Z_{i-\frac{1}{2}}}^{Z_{i+\frac{1}{2}}}\frac{\partial J}{\partial Z}dZdt=\int_{tk}^{tk+1}\int_{Z_{i-\frac{1}{2}}}^{Z_{i+\frac{1}{2}}}SCdZdt, \tag{12}$$

i.e.

$$(\hat{\rho}_i^{k+1}C_i^{k+1}-\hat{\rho}_i^kC_i^k)\Delta Z+(J_{i+\frac{1}{2}}^{k+\frac{1}{2}}-J_{i-\frac{1}{2}}^{k+\frac{1}{2}})\Delta t=S_i^{k+\frac{1}{2}}\cdot C_i^{k+\frac{1}{2}}\cdot\Delta Z\cdot\Delta t \tag{13}$$

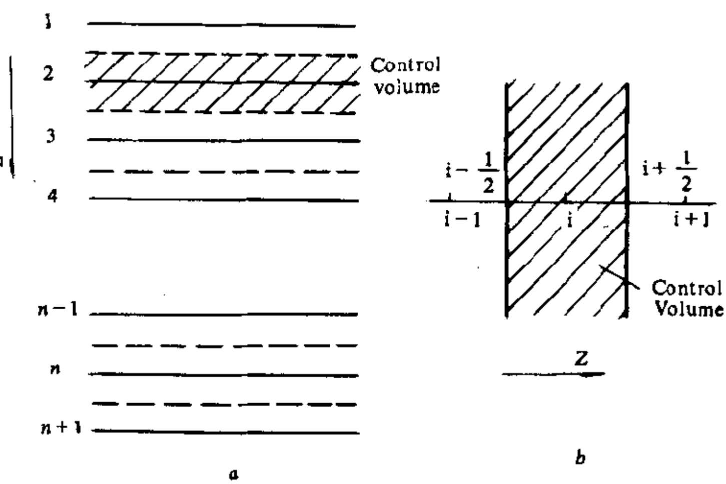

Fig.2 Control volume for one-dimensional case

During calculation of solute flux, central difference and up-wind difference or linear interpolation are used to solve dispersion term and convection term, respectively, according to the value of Pe ($=q\,\Delta Z/D_{sh}$, called as peclet number). Differential equation of J is given by:

$$J_{i+\frac{1}{2}}^{k+\frac{1}{2}}=\beta_1 q_{i-\frac{1}{2}}^{k+\frac{1}{2}} C_i^{k+1}+\beta_2 q_{i+\frac{1}{2}}^{k+\frac{1}{2}} C_{i+1}^{k+\frac{1}{2}}-(D_{sh})_{i+\frac{1}{2}}^{k+\frac{1}{2}} \frac{C_{i+1}^{k+\frac{1}{2}}-C_i^{k+\frac{1}{2}}}{\Delta Z} \tag{14}$$

$$J_{i-\frac{1}{2}}^{k+\frac{1}{2}}=\beta_3 q_{i-\frac{1}{2}}^{k+\frac{1}{2}} C_{i-1}^{k+\frac{1}{2}}+\beta_4 q_{i-\frac{1}{2}}^{k+\frac{1}{2}} C_i^{k+\frac{1}{2}}-(D_{sh})_{i-\frac{1}{2}}^{k+\frac{1}{2}} \frac{C_i^{k+\frac{1}{2}}-C_{i-1}^{k+\frac{1}{2}}}{\Delta Z} \tag{15}$$

when $|P_{e1}|=\left|\frac{q_{i-\frac{1}{2}}^{k+\frac{1}{2}}\cdot\Delta Z}{(D_{sh})_{i-\frac{1}{2}}^{k+\frac{1}{2}}}\right|\geqslant 2,\quad |P_{e2}|=\left|\frac{q_{i+\frac{1}{2}}^{k+\frac{1}{2}}\cdot\Delta Z}{(D_{sh})_{i+\frac{1}{2}}^{k+\frac{1}{2}}}\right|\geqslant 2,$

the up-wind difference method is used, i.e. the values of β_1, β_2, β_3, β_4 are given by when

$$q_{i+\frac{1}{2}}^{k+\frac{1}{2}}>0,\ \beta_1=1,\ \beta_2=0;\qquad q_{i+\frac{1}{2}}^{k+\frac{1}{2}}<0,\ \beta_1=0,\ \beta_2=1;$$

when

$$q_{i-\frac{1}{2}}^{k+\frac{1}{2}}>0,\ \beta_3=1,\ \beta_4=0;\qquad q_{i-\frac{1}{2}}^{k+\frac{1}{2}}<0,\ \beta_3=0,\ \beta_4=1; \tag{16}$$

Interpolating Equation (14) and Equation (15) into Equation (13), Equation (17) can be obtained

$$\hat{a}_i C_{i-1}^{k+1}+\hat{b}_i C_i^{k+1}+\hat{C}_i C_{i+1}^{k+1}=\hat{h}_i, \tag{17}$$

in which,

$$\hat{a}_i=\frac{1}{2}\left(-\beta_3 q_{i-\frac{1}{2}}^{k+\frac{1}{2}}-\frac{1}{\Delta Z}(D_{sh})_{i-\frac{1}{2}}^{k+\frac{1}{2}}\right),$$

$$\hat{b}_i=\frac{\Delta Z}{\Delta t}\hat{\rho}_i^{k+1}+\frac{1}{2}\left[\beta_1 q_{i+\frac{1}{2}}^{k+\frac{1}{2}}-\beta_4 q_{i-\frac{1}{2}}^{k+\frac{1}{2}}+\frac{1}{\Delta Z}\left((D_{sh})_{i-\frac{1}{2}}^{k+\frac{1}{2}}+(D_{sb})_{i+\frac{1}{2}}^{k+\frac{1}{2}}\right)+S_i^{k+\frac{1}{2}}\cdot\Delta Z\right],$$

$$\hat{C}_i=\frac{1}{2}\left(\beta_2 q_{i+\frac{1}{2}}^{k+\frac{1}{2}}-\frac{1}{\Delta Z}(D_{sh})_{i+\frac{1}{2}}^{k+\frac{1}{2}}\right),$$

$$\hat{h}_i=-\hat{a}_i C_{i-1}^k+\left[-\hat{b}_i+\frac{\Delta Z}{\Delta t}(\hat{\rho}_i^k+\hat{\rho}_i^{k+1})\right]C_i^k-\hat{C}_i C_{i+1}^k.$$

The boundary condition is similar to that in water flow submodel.

Using the discrete method mentioned above, a group of linear equations can be deduced for both water flow submodel and pesticide movement submodel

$$\begin{bmatrix} \hat{b}_1 & \hat{c}_1 & & & \\ \hat{a}_2 & \hat{b}_2 & \hat{c}_2 & & \\ & \ddots & \ddots & \ddots & \\ & & \hat{a}_{n-1} & \hat{b}_{n-1} & \hat{c}_{n-1} \\ & & & \hat{a}_n & \hat{b}_n \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_{n-1} \\ c_n \end{bmatrix} = \begin{bmatrix} \hat{h}_1 \\ \hat{h}_2 \\ \vdots \\ \hat{h}_{n-1} \\ \hat{h}_n \end{bmatrix} \tag{18}$$

Linear equations are triangular equations which can be solved by using Gauss elimination or Thomas' method. The calculation flow chart is shown in Fig. 3.

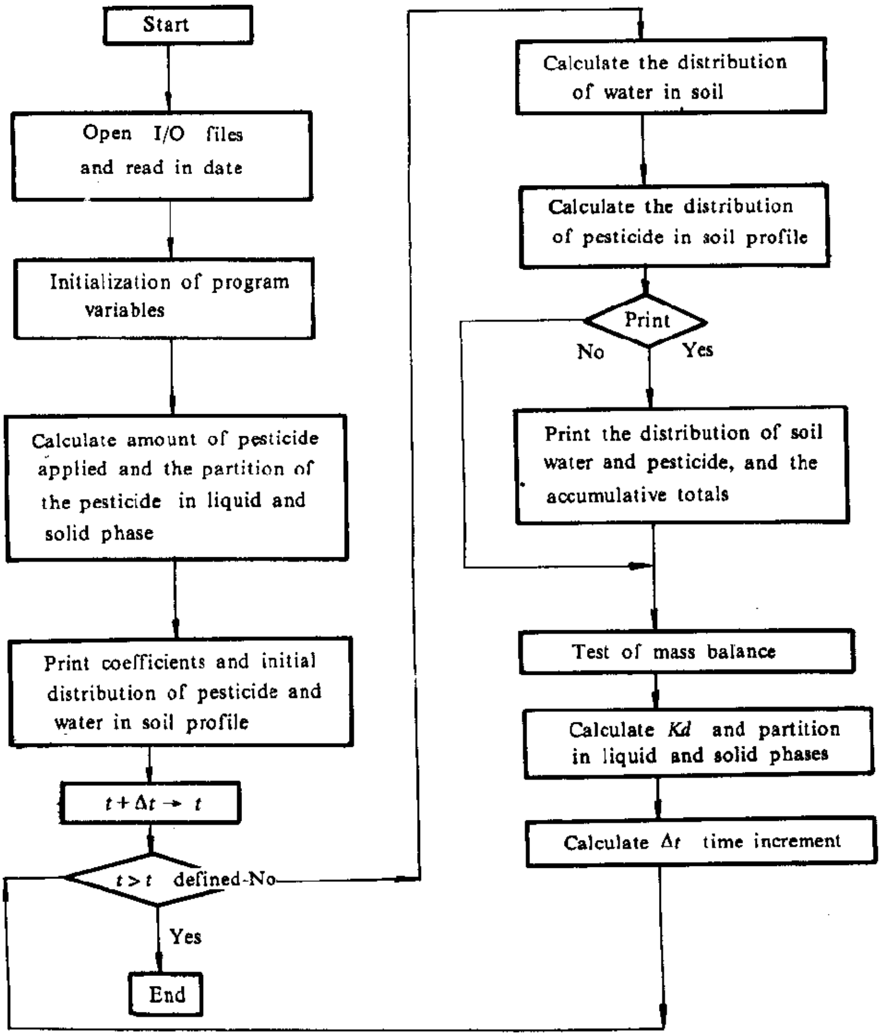

Fig. 3 Flow chart of the model

TEST OF THE MODEL

Numerical simulation for the leaching of CCU in two soil columns were carried out. Soil samples were taken from top soil of vegetable field in Beijing. The content of organic matter in soil was 2.75% and pH value was 8.54. Measurements showed that the coefficients of soil water are as follows:

water diffusion coefficients of unsaturated soil:

$$D(\theta)=\begin{cases} 0.08747\theta^{1.8586} & \theta<0.1539 \\ 62.2093\theta^{5.3682} & 0.1539\leqslant\theta<0.4485\ \mathrm{cm^2/min} \\ 6.5253\cdot 10^{4}\theta^{14.0416} & \theta\geqslant 0.4485. \end{cases} \tag{19}$$

Water conductivity of unsaturated soil:

$$K(\theta)=5.9215\cdot 10^{-9}\, e^{30.1521\theta}\ \mathrm{cm/min}. \tag{20}$$

The adsorption of CCU in the soil is described by the equation:

$$C_s=37.2\ C^{0.704}, \tag{21}$$

where, units of C_s and C are $\mu g/g$ and $\mu g/cm^3$, respectively. Half life of CCU in the soil was 14.54 days .

In the experiments, arid soil bulk density was 1.2 g/cm^3, initial water content in the soil profile was uniform. The cross section area of column A was 87.3 cm^2, initial water content was 0.08 cm^3/cm^3, total rainfall was 1510 cm^3, leaching time was 29.5 hours and applied amount of CCU was 25.5 mg. In column B, the across section area was 83.34 cm^2, initial soil water content was 0.105 cm^3/cm^3, total rainfall was section 1553 cm^3, leaching time was 34.67 hours, and applied amount of CCU was 15.0 mg. The hydrodynamic dispersion coefficient is calculated from the results in column A, and given by

$$D_{sh}(\theta.q)=6.0\ |q|+0.8\times 10^{-3}\times 0.003e^{10\theta}\ \mathrm{cm^2/min}. \tag{22}$$

Simulation results and measured data for column A and B are compared in Fig. 4 and Fig. 5. The figures show clearly coincidence simulation of the results with those measured indicating reliability of the model.

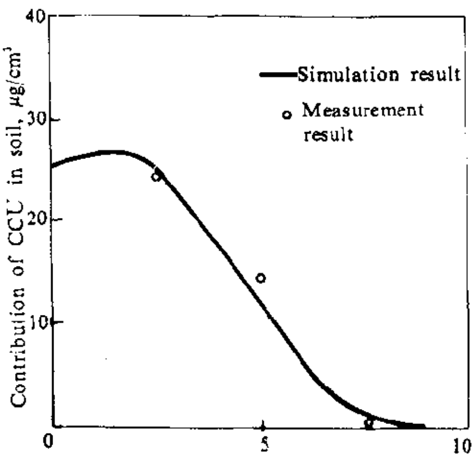

Fig. 4 Distribution of CCU in column A (t=25.9 hours)

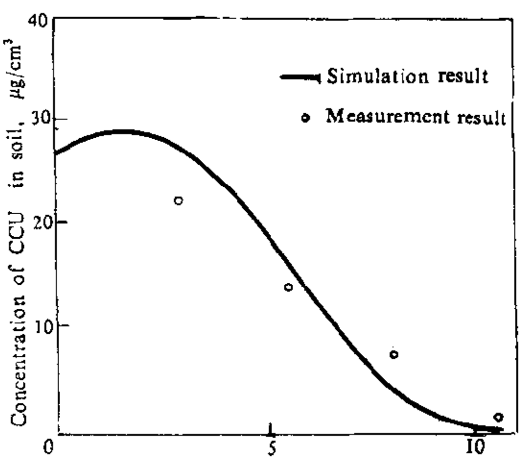

Fig. 5 Distribution of CCU in column B (t=34.67 hours)

APPLICATION OF THE MODEL

In order to simplify the problem, following assumptions were made: the soil was homogenous; the initial soil water was also homogeneous and the water content was $0.2cm^3/cm^3$; the application rate of CCU was 150 g/ha and all the pesticide was applied to the soil surface; the rainfall with a rate of 4.8 min/h began immediately after the application of CCU, and evaporation with a rate of 3.55 mm/d began two days later; and the duration of the process under consideration was one week.

The soil water coefficients are given by

(1) water diffusion rate of unsaturated soil

$$D(\theta) = \begin{cases} 2.68420\theta^{1.0504} & \theta < 0.26133 \\ 2.9854 \cdot 10^{6}\theta^{11.4246} & \theta \geq 0.26133 \end{cases} \quad cm^2/min \tag{23}$$

(2) water conductivity of unsaturated soil.

$$K(\theta) = 2.9757 \times 10^{-6}\, e^{24.20730\theta}\ cm/min \tag{24}$$

The adsorption of CCU in the soil is described

$$C_s = 12.33\ C^{1.00} \tag{25}$$

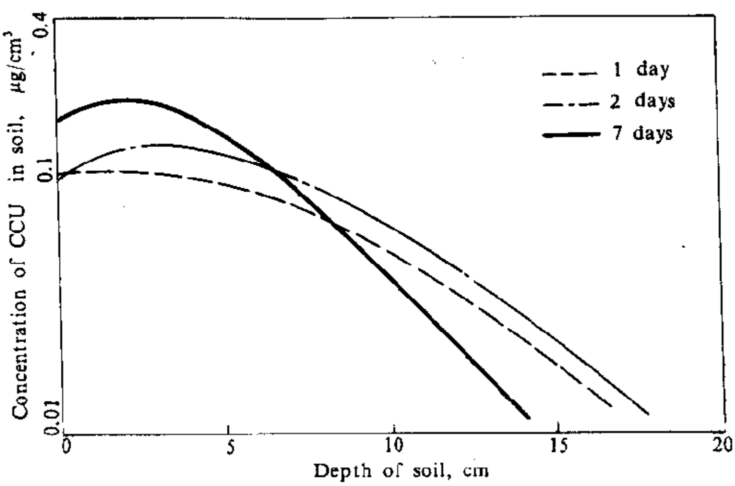

Fig. 6 Distribution of CCU in soil profile

The half life of CCU in the soil was 15 days. Simulation results listed in Table 1 and Fig.6 show that most of the residues of CCU retained in the soil layer of 0 – 12 cm and the maximum leaching depth was 30 cm, it indicated that CCU possessed a weak tendency of leaching to the deep layer of soil and to the ground water. It is also demonstrated that CCU moved very slowly for the duration of evaporation of soil water.

Table 1 Persistence and distribution of CCU in soil profile

	Mi/Mt						*Mt/Mo*
Depth, cm	0 – 4	4 – 8	8 – 12	12 – 16	16 – 20	20 – 30	Total
1 day	0.496	0.335	0.120	0.035	0.014	0.00	0.960
2 days	0.340	0.327	0.189	0.084	0.034	0.026	0.918
3 days	0.343	0.318	0.187	0.086	0.036	0.030	0.830
4 days	0.354	0.311	0.185	0.085	0.036	0.029	0.725

Notes: *MO*— total initial applied amounts of CCU; *Mt* — total residue of CCU in soil; *Mi* — residue of CCU in soil for each layer.

SUMMARY

A numerical simulation model which can describe pretty well the transport and transformation of pesticides in unsaturated soil is developed. It is very simple and effective and the approach can be expanded to predict the fate of pesticide under field conditions.

REFERENCES

Carsel, R.F., Mulkey, L.A., Lorber M N. and Baskin, L.B., Ecologicɑl Modelling, 1985, 30: 49

Lei Zhidong, Yang Shixiu and Zhuan Xishen, Dynamics of soil water, Beijing: Tsinghua University Press, 1988

Nielsen, D.R., Ven Genuchten, M.TH. and Bigger, J.W., Water Resour. Res., 1986, 22: 895

Wagenet, R.J. and Hutson, J.L., J. Environ. Qual., 1986, 15: 315

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