Numerical analysis of field-scale transport of bromacil

David Russo a, Inbar Tauber-Yasur b, Asher Laufer a & Bruno Yaron b

a Department of Soil Physics, Institute of Soils and Water, Agricultural Research Organization, The Volcani Center, Bet Dagan 50250, Israel
b Department of Soil Residue Chemistry, Institute of Soils and Water, Agricultural Research Organization, The Volcani Center, Bet Dagan 50250, Israel

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Field-scale transport of bromacil (5-bromo-3-sec-butyl-6-methyluracil) was analyzed using two different model processes for local description of the transport. The first was the classical, one-region convection dispersion equation (CDE) model while the second was the two-region, mobile–immobile (MIM) model. The analyses were performed by means of detailed three-dimensional, numerical simulations of the flow and the transport [Russo, D., Zaidel, J. and Laufer, A., Numerical analysis of flow and transport in a three-dimensional partially saturated heterogeneous soil. Water Resour. Res., 1998, in press] 1, employing local soil hydraulic properties parameters from field measurements and local adsorption/desorption coefficients and the first-order degradation rate coefficient from laboratory measurements. Results of the analyses suggest that for a given flow regime, mass exchange between the mobile and the immobile regions retards the bromacil degradation, considerably affects the distribution of the bromacil resident concentration, \( c \), at relatively large travel times, slightly affects the spatial moments of the distribution of \( c \), and increases the skewing of the bromacil breakthrough and the uncertainty in its prediction, compared with the case in which the soil contained only a single (mobile) region. Mean and standard deviation of the simulated concentration profiles at various elapsed times were compared with measurements from a field-scale transport experiment [Tauber-Yasur, I., Hadas, A., Russo, D. and Yaron, B., Leaching of terbuthylazine and bromacil through field soils. Water, Air Soil Poln., 1998, in press] 2 conducted at the Bet Dagan site. Given the limitations of the present study (e.g. the lack of detailed field data on the spatial variability of the soil chemical properties) the main conclusion of the present study is that the field-scale transport of bromacil at the Bet Dagan site is better quantified with the MIM model than the CDE model. © 1998 Elsevier Science Limited. All rights reserved

1 INTRODUCTION

Large volumes of potentially hazardous chemicals, produced by various industries and by agricultural operations, are entering the ecosystem. Quantitative descriptions of chemical transport in the vadose (unsaturated) zone on the field scale are, therefore, essential for predicting the behavior of these chemicals in the ecosystem. Towards this goal a transport experiment was recently concluded on a field plot at Bet Dagan, Israel 2. The experiment was analyzed by a relatively simple, one-dimensional stochastic model 3, based on ensemble mean statistics, restricted by several simplifying assumptions regarding the local flow regime, and the statistics and structure of the soil heterogeneity.

Most of these limitations may be overcome with a numerical approach that combines a statistical generation method to produce realizations of the heterogeneous soil properties at sufficient resolution, with an efficient numerical method to solve the partial differential equations governing flow and transport in unsaturated soils, described as a two-dimensional 4–7 or a three-dimensional 8 problem.

The purpose of the present study is twofold: firstly, to analyze the transport of an organic chemical on the field

*Corresponding author.
scale by means of two different model processes; and secondly, to use the results of these analyses to investigate the mechanisms controlling the transport of this chemical through the unsaturated zone on the field scale. To do so we employ detailed three-dimensional, numerical simulations of flow and transport. Comparison of the simulation results with the available experimental transport data is used to assess the applicability of the different model processes for describing bromacil transport at the Bet Dagan field.

2 THE FIELD EXPERIMENT

A detailed description of the experimental plot, the experimental methodology, and the measurements is given in Tauber-Yasur et al. and Russo et al. For the sake of completeness we give here a brief outline with emphasis on the data needed in our present analysis. The transport experiment was carried out on a plot of $20 \times 6$ m at Bet Dagan. The soil is a sandy loam and the plot was bare. Bromacil (5-bromo-3-sec-butil-6-methyluracil) was applied on the surface ($5.5 \text{ g m}^{-2}$) by hand-spraying. Water was applied by a few irrigation sessions and from rainfall. Disturbed soil samples were taken from 20 locations randomly selected within the plot. At each location the samples were taken at four to six depths and on four occasions, the last being 251 days after solute application. To minimize destruction, the exact locations of the sampling points were slightly changed each time. Solute concentrations were determined in the laboratory after chemical extraction from the soil samples.

Kinetics of adsorption and desorption for bromacil were determined experimentally on 20 samples. Equilibrium was reached after 24 h, but most of the adsorption was completed after 4 h. Hysteretic behavior was observed and the average partition coefficients, $K_d$ were 0.7 cm$^3$ g$^{-1}$ at adsorption and 1.7 cm$^3$ g$^{-1}$ after desorption. In addition measurements of two soil properties, saturated conductivity, $K_s$ and the soil parameter $\alpha$, viewed as the reciprocal of the macroscopic capillary length scale were carried out at 130 sampling points. This led to the identification of the statistical parameters characterizing the spatial variability of $K_s$ and $\alpha$, which indicates that part of this variability results from a deterministic trend rather than a random variation.

3 ANALYSIS OF THE FIELD-SCALE TRANSPORT

The transport problem is analyzed by means of a physically based flow and transport model and a stochastic presentation of the soil properties that affect water flow and solute transport. The ‘single realization’ approach undertaken here may be understood as quantifying the macroscopic spreading of a single plume for particular site-specific applications.

3.1 Governing partial differential equations

Water flow is described locally by the Richards equation, the physical parameters of which are visualized as realizations of random space functions (RSFs). Two different process models are adopted here for local description of the transport. The first is the classical, one-region convection-dispersion equation (CDE) model while the second is the two-region, mobile–immobile (MIM) model. The reactive solute may exchange with the solid phase of the soil and may undergo degradation (chemical or biological) in both liquid and solid phases. The exchange of solute between solid and liquid phases is not completely reversible and is described by an adsorption isotherm which differs from the desorption isotherm.

In a Cartesian coordinate system, assuming local isotropy, the ‘mixed’ form of the Richards equation governing saturated-unsaturated flow is:

$$\frac{\partial \theta}{\partial t} = \sum_{i=1}^{3} \frac{\partial}{\partial x_i} \left[ K_{i} \frac{\partial \theta}{\partial x_i} - \frac{\partial K}{\partial x_i} \right]$$

where $\theta = \theta(x,t)$ [m$^3$ water/m$^3$ soil] is the volumetric water content; $\psi = \psi(x,t)$ [m water] is the pressure head; $K = K(\psi, x)$ [m/d] is the hydraulic conductivity (scalar); $x = (x_1, x_2, x_3)$ [m] is the spatial coordinate vector ($x_i$ is directed vertically downwards) and $t$ [d] is time.

If we assume linear adsorption and desorption isotherms for the partitioning of the solute between the solid and liquid phases and a first-order degradation in both phases, the governing partial differential equation of the reactive solute is:

$$\frac{\partial [\theta + \rho_S K_d c]}{\partial t} = \sum_{i=1}^{3} \sum_{j=1}^{3} \frac{\partial}{\partial x_i} \left[ D_{ij} \frac{\partial c}{\partial x_j} \right]$$

- $\sum_{i=1}^{3} \frac{\partial u_i \phi_i}{\partial x_i} - \mu (\theta + \rho_S K_d c)$

where $c$ [kg m$^{-3}$] is the aqueous solute concentration; $K_d$ [m$^2$ kg$^{-1}$] is the local (hysteretic) liquid/solid partitioning coefficient; $\rho_S$ [kg m$^{-3}$] is the bulk density; $D_{ij}$ [m$^2$ d$^{-1}$] ($i,j = 1,2,3$) are components of the pore water velocity vector; and $D_{ij}$ [m$^2$ d$^{-1}$] ($i,j = 1,2,3$) are components of the pore-scale dispersion tensor, given as:

$$D_{ij} = (\lambda_\perp |u_i| + D) \delta_{ij} + (\lambda_T - \lambda_\perp) u_i u_j / |u|$$

where $\lambda_\parallel$ and $\lambda_T$ [m] are the longitudinal and the transverse pore-scale dispersivities; $\delta_{ij}$ is the Kronecker delta; $|u| = \left( |u_1|^2 + |u_2|^2 + |u_3|^2 \right)^{1/2}$; and $D$ [m$^2$ d$^{-1}$] is the effective molecular diffusion coefficient, given as:

$$D = D_0 (\theta^{1/3})$$

where $D_0$ [m$^2$ d$^{-1}$] is the molecular diffusion coefficient in water and $\theta$ is the saturated volumetric water content.

Similarly, the equation governing the two-region,
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Mobile–immobile transport of the reactive solute is:

\[
\frac{\partial(\theta_m + f p_w K_d c_m) + \partial(\theta_m + (1-f)p_w K_d c_m)}{\partial t} = \sum_{i=1}^{3} \sum_{j=1}^{3} \frac{\partial}{\partial x_j} \left[ \theta_m D_{ij} \frac{\partial c_m}{\partial x_j} \right] - \mu \left[ (\theta_m + f p_w K_d c_m) c_m + (\theta_m + (1-f)p_w K_d c_m) \right]
\]

where subscripts \( m \) and \( im \) denote the mobile and immobile regions; \( f \) is the mass fraction of sorbent in the mobile region, selected here as \( f = (\theta_m, \theta_m) \theta_m \); \( D_{ij} \) is given by eqn (3) with \( D_m \), the effective molecular diffusion coefficient in the fluid mobile region, replacing \( D \), \( \gamma \) \((d^{-1})\) is the first-order mass transfer coefficient representing solute diffusion between the mobile and the immobile fluid regions, calculated from:

\[
\gamma = 150 \mu D_m / \eta_n
\]

where \( \theta_m \) is the immobile water content, selected here as \( \theta_m = \theta_m \), where \( \theta_m \) is the residual volumetric water content at which \( K \rightarrow 0 \), \( D_m \) is the effective molecular diffusion coefficient in the immobile zone (given by eqn (3) with \( \theta_m \) replacing \( \theta \) and \( D_m \) replacing \( D \)) and \( r_a \) \([m]\) is the average radius of a soil aggregate.

Note that at the small \( \gamma \) limit, \( \gamma \rightarrow 0 \), there is no mass transfer to the immobile region, i.e. \( c_m = 0 \) and eqns (4a) and (4b) reduces to the one-region CDE eqn (2) with \( c = c_m \) and \( \theta = \theta_m \). On the other hand, at the large \( \gamma \) limit, \( \gamma \rightarrow \infty \), physical equilibrium between the two regions is reached, i.e. \( c_m = c_m \) and eqns (4) and (4) reduces to eqn (2) with \( c = c_m \) and \( \theta = \theta_m + \theta_m \).

3.2 Characterization of the flow and transport parameters

The properties of the soil and/or the chemicals that are here hypothesized to control the field-scale solute spread are the soil hydraulic properties, characterized by the \( K(\psi) \) and the \( \theta(\psi) \) relationships, the partitioning coefficient, \( K_d \), the first-order degradation rate coefficient \( \mu \); and, in the case of the mobile–immobile flow model, the first-order mass transfer coefficient, \( \gamma \). These soil properties vary in space in an irregular fashion, on length scales much greater than the pore scale. Our main concern is the effect of their spatial variations on solute transport. Deterministic, constant values were adopted for pore-scale dispersivities, \( \lambda_1 = 2 \times 10^{-5} \) m and \( \lambda_2 = 1 \times 10^{-7} \) m, the bulk density of the soil, \( \rho_b = 1400 \) kg m\(^{-3}\); the molecular diffusion coefficient in water, \( D_w = 5.4 \times 10^{-5} \) m\(^2\) s\(^{-1}\); and the average radius of a soil aggregate, \( r_a = 0.005 \) m.

To simplify the analysis and in line with the field data it is assumed that the local \( K(\psi) \) and \( \theta(\psi) \) relationships are given by the Gardner–Russo model.\(^{16,17}\) Ignoring hysteresis and local anisotropy, and considering the pressure head, \( \psi \), as the dependent variable, we have:

\[
K(\psi, x) = K_x(x) \exp[-\alpha(x) / \psi]
\]

\[
\Theta(\psi, x) = \left\{ \exp \left( \frac{1}{2} \alpha(x) / \psi \right) \right\} \left[ 1 + \frac{1}{2} \alpha(x) / \psi \right] \right\} \theta_x(\psi) \right\}
\]

where \( n \) is a soil parameter selected\(^18\) as \( n = 0 \), and \( \Theta = (\theta_x - \theta_x) / (\theta_x - \theta_x) \) is the effective water saturation. Furthermore, it is assumed here that the parameters \( K_x \), \( \alpha \), \( \theta_x \), and \( \theta_x \) in eqns (6a), (6b) and the coefficients \( K_d, \mu \) and \( \gamma \) in eqn (2) and eqns (4a) and (4b), denoted by \( p(x) \), are described by the general model:

\[
p(x) = m(x) + w(x)
\]

where \( m(x) \) is a priori mean or drift function, and \( w(x) \) is a zero mean, second-order stationary RSF, characterized completely by a covariance function, \( C_{ww}(x, x') \) that depends on the separation vector \( x = x - x' \), and not on \( x \) and \( x' \) individually.

In line with the field observations\(^8,19\) of the parameters in eqns (6a) and (6b), appropriate models for \( m(x) \) and \( C_{ww}(x, x') \) are the general linear model eqn (7b) and the exponential model eqn (7c), respectively, i.e.:

\[
m(x) = \sum_{i=0}^{k-1} \beta_i f(x)
\]

\[
C_{ww}(x, x') = \sigma_w^2 \exp(-|x - x'|)
\]

where \( f(x), i = 1 \) to \( k - 1 \) are known polynomial functions of the spatial coordinate vector \( x, k = (\ell + 1)(\ell + 2) / 2 \) is the space dimension, \( \ell \) is the order of the polynomial, \( f_d(x) = 1 \), and \( \beta_i, i = 0 \) to \( k - 1 \), are the drift parameters Table 1; \( x' = (x - x') \) is the scaled separation vector, \( x' = |x' - x'| ; \) and \( \sigma_w^2 \) and \( L_w = (I_{f_d}, j_{f_d}, L_{f_d}) \) are the variance and correlation scales of \( w(x) \), respectively, Table 1.

Statistics of the parameters in eqns (6a) and (6b) for the Bet Dagan soil are given elsewhere\(^8,19\). Detailed information on the spatial distribution of \( K_d \) and \( \mu \) in the Bet Dagan field is, however, not available. Assuming that \( K_d \) and \( \mu \) are log-normally distributed, the mean value and the variance of the general model eqn (7) were estimated from a series of laboratory tests using bromacil and Bet Dagan soil\(^20\). Similar to Burr et al,\(^21\) the covariance model eqn (7c) and the correlation scales of \( \log K_d \) were adopted for \( m(x) \) and \( \log \mu \).

3.3 Generation of the flow and transport parameters field

Generation of conditional random realizations of the flow and transport parameters field is most appropriate for our purpose. This task can be accomplished by the method of conditional simulation\(^22\). Application of the method to the log \( K_d \) and log \( \alpha \) field in the Bet Dagan site is demonstrated elsewhere\(^8\). The limited data on the spatial distribution of
Table 1. Statistical parameters of the spatially variable soil properties log $K$, log $\theta$, and log $\mu$ and log $\gamma$

<table>
<thead>
<tr>
<th>$\sigma^2$</th>
<th>log $K_s$</th>
<th>log $\alpha$</th>
<th>$\theta_s$</th>
<th>$\theta_r$</th>
<th>log $K^2_s$</th>
<th>log $K_j$</th>
<th>log $\mu$</th>
<th>log $\gamma^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.495</td>
<td>0.266</td>
<td>0.003</td>
<td>0.024</td>
<td>0.320</td>
<td>0.315</td>
<td>0.305</td>
<td>0.345</td>
<td></td>
</tr>
<tr>
<td>$I_{ov}$ (m)</td>
<td>0.218</td>
<td>0.143</td>
<td>0.165</td>
<td>0.177</td>
<td>0.218</td>
<td>0.218</td>
<td>0.218</td>
<td>0.177</td>
</tr>
<tr>
<td>$I_{ov}$ (m)</td>
<td>0.872</td>
<td>0.488</td>
<td>0.463</td>
<td>0.621</td>
<td>0.872</td>
<td>0.872</td>
<td>0.872</td>
<td>0.621</td>
</tr>
<tr>
<td>$\beta^0$ (m$^{-1}$)</td>
<td>0.798</td>
<td>0.453</td>
<td>0.451</td>
<td>0.590</td>
<td>0.798</td>
<td>0.798</td>
<td>0.798</td>
<td>0.590</td>
</tr>
<tr>
<td>$\beta^0$ (m$^{-1}$)</td>
<td>1.818</td>
<td>-2.945</td>
<td>0.375</td>
<td>0.102</td>
<td>-7.512</td>
<td>-6.520</td>
<td>-6.210</td>
<td>-4.001</td>
</tr>
<tr>
<td>$\beta^0$ (m$^{-1}$)</td>
<td>-1.383</td>
<td>-0.011</td>
<td>-0.011</td>
<td>-1.212</td>
<td>-0.815</td>
<td>-1.225</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* $K_s$ is given in m$^{d-1}$, $\alpha$ is given in m$^{-1}$, $K_j$ is given in m$^{d-1}$ kg$^{-1}$, and $\mu$ and $\gamma$ are given in d$^{-1}$
* $a$ at adsorption
* $b$ after desorption
* $c$ at adsorption
* $d$ is calculated from eqn (5)

Using eqns (6a) and (6b), one-dimensional tables of relative conductivity, $K'_s = K/K_s$ and relative water content, $\theta'_i = (\theta - \theta_i)/(\theta - \theta_i)$ were constructed as functions of $\alpha'_i = (\alpha - 1)\delta_{i\omega}$ where $\alpha' = \alpha/\psi$, $\psi = 1$ to $n_{\omega}$, $\delta_{i\omega} = 50/000$ and $b_s = 0.01$. Employing a linear interpolation scheme, these tables were used to calculate values of $K'$ and $\theta = \theta'(\theta - \theta_i)/\theta_i$ for each cell of the flow domain by means of the generated realizations of log $\alpha$, $\theta_i$, and $\theta_i$ and the simulated water pressure head, $\psi$. Hydraulic conductivity between cells, the so-called interblock conductivity, was estimated from the generated realization of $K_s$ and the calculated $K'_s$ using the asymptotic weighting (AW) scheme proposed by Zaidel and Russo.

Values of the mass transfer coefficient, $\gamma$ were generated from eqn (5), by means of the generated realizations of $\theta_i$ and $\theta_i$ and the constants $h$ and $D_i$. Values of $K_j$ at adsorption and after desorption were generated from eqn (7) using the generated realization of $K_i$ and the relevant statistical parameters Table 1.

### 3.4 Boundary and initial conditions

We considered the movement of bromacil in a flow domain consisting of a heterogeneous soil with a prescribed initial capillary pressure head, $\psi(x) = \psi(\theta(t))$. Water is infiltrated into the soil as a time-dependent flux, $q(t) > 0$, imposed on the entire soil surface. Water may leave the flow system through the upper boundary ($x_1 = 0$) by evaporation ($q(t) < 0$) and through the lower boundary ($x_3 = L_3$) by gravity flow. There is no water flow across the vertical planes located at $x_2 = 0$, $x_2 = L_2$, $x_1 = 0$ and $x_3 = L_3$, for which the normal derivatives of $c$ vanish. In addition, zero-gradient-boundary is specified for $c$ at the bottom ($x_1 = L_1$). For water flow, the boundary and initial

The relevant chemical parameters in this site, however, precludes the generation of conditional random realizations of the chemical parameters field. Consequently, only unconditional random realizations of the flow and transport parameters field were generated in the present study.

The flow domain which measures $L_1 = 2$ m in the vertical direction and $L_2 = 22$ m and $L_3 = 7.5$ m in the horizontal directions, was discretized into a grid of 40 x 88 x 30 equalized cells, measuring 0.05 m and 0.25 m in the vertical and horizontal directions, respectively. By means of the covariance model eqn (7) and the values of $\sigma^2$ and $I_v$ Table 1, the turning bands method was used to generate independent, unconditional realizations of the residuals, $w(x)$ of log $K_s$, log $\alpha$, and log $\mu$ on each of the nodes of the flow domain grid. Employing eqn (7), the resultant realizations of $w(x)$ and the deterministic drift, $m(x)$ eqn (7) were used to generate realizations of $p(x)$ for log $K_s$, log $\alpha$, and log $\mu$, respectively, on each of the nodes of the domain grid.

Considering the physically plausible situation in which log $K_s$ and $\theta_i$ are negatively correlated with log $K_s$, and log $\alpha$ and $\theta_i$ are positively correlated with log $K_s$, the realizations of log $K_s$, log $\alpha$, and $\theta_i$ and $\theta_i$ were generated from that of log $K_s$ via the relationship:

$$g(x) = m_s(x) + (log K_s(x) - m_s(x))(\rho_{\alpha} \sigma_{\alpha} \rho_{\alpha} \rho_{\alpha} \sigma_{\alpha} \rho_{\alpha})^{1/2}$$

where $g = log K_s$, log $\alpha$, or $\theta_i$, $m(x)$, $\sigma^2$, and $\rho$ are the mean and variance of log $K_s$, and $\rho$ is the cross-correlation coefficient between log $K_s$ and $g$, and $R_N$ is a random number taken from the normal distribution $N(0,1)$.

Cross-correlation coefficients for Bet Dagan soil, $\rho$, for $g = log \alpha$, $\theta_i$, and $\theta_i$, were adopted from Russo and Bouton. Unfortunately, information on the cross-correlation between log $K_s$ and log $K_j$ for the Bet Dagan soil is not available. In line with the findings of Robin et al., we considered a (moderately) negative cross-correlation coefficient, i.e. $\rho(\log d) = -0.5$. For water flow, the boundary and initial
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and initial conditions are:

\[-K(\psi) \frac{\partial \psi}{\partial x_1} + K(\psi) \leq |q_0(t)|, \quad x_1 = 0, \quad 0 \leq x_2 \leq L_2,\]

\[0 \leq x_3 \leq L_3, \quad t > 0\]  

(8a)

\[\frac{\partial \psi}{\partial x_1} = 0, \quad x_1 = L_1, \quad 0 \leq x_2 \leq L_2, \quad 0 \leq x_3 \leq L_3, \quad t > 0\]  

(8b)

\[-K(\psi) \frac{\partial \psi}{\partial x_2} = 0, \quad x_2 = 0, \quad x_3 = L_3, \quad 0 \leq x_1 \leq L_1, \quad t > 0\]  

(8c)

\[\frac{\partial \psi}{\partial x_2} = 0, \quad x_2 = 0, \quad x_3 = L_3, \quad x_1 \leq x_1 \leq L_1, \quad t > 0\]  

(8d)

\[\psi = \psi(x), \quad 0 \leq x_1 \leq L_1, \quad 0 \leq x_2 \leq L_2, \quad 0 \leq x_3 \leq L_3, \quad t = 0\]  

(8e)

while for the one-region (mobile) transport, the boundary and initial conditions are:

\[c = c_0, \quad t = 0, \quad l_{11} \leq x_1 \leq l_{12}, l_{12} \leq x_2 \leq l_{22}, l_{31} \leq x_1 \leq l_{32}\]  

(9a)

\[c = 0, \quad t = 0, \quad 0 \leq x_1 \leq l_{11}, \quad l_{12} \leq x_1 \leq L_1\]  

(9b)

\[0 \leq x_2 \leq l_{21}, \quad l_{22} \leq x_2 \leq L_2\]  

(9c)

\[0 \leq x_3 \leq l_{11}, \quad l_{22} \leq x_3 \leq L_3\]  

(9d)

\[-\theta \sum_{j=1}^{3} D_{ij} \frac{\partial c}{\partial x_j} + \eta \cdot \frac{\partial c}{\partial t} = 0, \quad x_1 = 0, \quad 0 \leq x_2 \leq L_2, \quad t > 0\]  

(9e)

\[\frac{\partial c}{\partial x_2} = 0, \quad x_2 = 0, \quad x_2 = L_2, \quad 0 \leq x_1 \leq L_1, \quad 0 \leq x_3 \leq L_3, \quad t > 0\]  

(10a)

\[\frac{\partial c}{\partial x_5} = 0, \quad x_2 = 0, \quad x_2 = L_2, \quad 0 \leq x_1 \leq L_1, \quad t > 0\]  

(10b)

\[\frac{\partial c}{\partial x_5} = 0, \quad x_3 = 0, \quad x_3 = L_3, \quad 0 \leq x_1 \leq L_1, \quad 0 \leq x_2 \leq L_2, \quad t > 0\]  

(10c)

\[c_{im} = 0, \quad 0 \leq x_1 \leq L_1, \quad 0 \leq x_2 \leq L_2, \quad 0 \leq x_3 \leq L_3, \quad t = 0\]  

(10d)

Details of the numerical approach used to approximate the governing eqns (1) and (2) are given in Russo et al. The numerical scheme for the CDE model (eqn (2) subject to eqns (9a), (9b), (9c), (9d) and (9e)) was modified in order to solve the MIM model (eqns (4a) and (4b) subject to eqns (9a), (9b), (9c), (9d) and (9e) with $c = c_{im}$ and eqns (10a), (10b), (10c) and (10d)). In order to account for the hysteretic behavior of $K_p$ a hysteresis code was assigned to each numerical cell to determine which of the following conditions applied during the previous time step: (i) on the desorption isotherm; (ii) adsorption on a scanning isotherm; (iii) desorption on a scanning isotherm; and (iv) on the adsorption isotherm. Using this code a determination was made whether the same conditions applied for the current time step. If the conditions have changed, the appropriate code is assigned. The slopes of the (linear) scanning isotherms were somewhat arbitrary except for the restriction that they were smaller than the slopes of the adsorption or the desorption isotherms.

Actual irrigation/rain dates, rates and amounts with total cumulative amount of applied water ($W = 0.9$ m) were considered in the flow and transport simulations which proceeded for 251 days.

3.5 Quantification of the simulated solute spreading and breakthrough

To quantify the solute transport associated with the two different process models, the results of the transport simulations are expressed in terms of integrated measures of the solute transport, such as the spatial moments of the distribution of the point values of the solute concentration, and the solute breakthrough through a horizontal control plane (CP) located at an arbitrary vertical distance from the soil surface.

The spatial moments of the distribution of the resident concentration, $c$, given as mass per volume of soil solution, are given[20] as:

\[M(t) = \int \theta(x,t)c(x,t)dx\]  

(11a)
4 RESULTS AND DISCUSSION

4.1 Plumes of the simulated bromacil concentration

The irregular, ostensibly erratic, spatial variation of the simulated bromacil resident solute concentration, $c$ (Fig. 1) is due to the small-scale variability in both the physical and the chemical properties of the heterogeneous soil. At $t = 32$ days ($W = 0.2$ m), when the center of mass of the plume has traveled only a relatively small distance, the plume exhibits a limited spread in both the vertical longitudinal and the horizontal transverse directions. As time elapses ($t = 109$ days and $W = 0.72$ m) and the center of mass of the plume is displaced further, the plume evolves and exhibits a significant spread in the longitudinal direction and its accompanying dilution, while only limited horizontal transverse spreading is evident.

Comparison of the simulated solute plumes depicted in Fig. 1 reveals that generally, under the same flow conditions, the solute plumes associated with the CDE model Fig. 1(a) and (c) exhibit less spreading than those associated with the MIM model Fig. 1(b) and (d). This pattern is also shown in Fig. 2(c) and (d) below, which display the longitudinal and transverse components of the spatial covariance tensor, $S_{ij}$ eqn (11) for the two different transport models.

4.2 Spatial moments of the simulated bromacil plumes

It is clear from Fig. 1 that the point values of bromacil concentration are subject to a large uncertainty, attributed to the complex heterogeneity of the soil physical and chemical properties. Here we focus our attention on the spatial moments of the distribution of the point values of $c$ eqns (11a), (11b) and (11c). These larger-scale, integrated measures of the solute transport are subject to a much

\[
R(t) = \frac{1}{M}\int \theta(x) c(x,t) dx \tag{11b}
\]

\[
S_{ij}(t) = \frac{1}{M}\int \theta(x) c(x,t)[x_i - R_j(t)][x_j - R_j(t)] dx \tag{11c}
\]

where $M$ is the total mass of the solute, $R(t) = (R_x, R_y, R_z)$ is the coordinate of the centroid of the solute plume, and $S_{ij}(t)$ ($ij = 1, 2, 3$) are second spatial moments, proportional to the moments of inertia of the plume.

The solute breakthrough curve (BTC) is calculated from the flux-averaged concentration, $c_i$, defined\(^\dagger\) as:

\[
c_i(x,t) = \frac{\int \theta(x,t) u(x,t) s(x,t) dA}{\int \theta(x,t) u(x,t) dA} \tag{12a}
\]

where $s$ and $u$ are the solute flux and the velocity vectors, respectively, with $s = s \cdot n$ and $u = u \cdot n$ being the mass of solute and the volume of water per unit time and unit area moving through a surface element of unit normal $n$, and water content, $\theta$ and the integration is over a planar area $A$.

Mean and standard deviation of the simulated bromacil BTC are evaluated by averaging $c_i$ over a given horizontal CP located at an arbitrary vertical distance $\Xi$ from the soil surface, i.e.:

\[
\langle c_i(\Xi,t) \rangle = (L_2L_3)^{-1} \int_0^{L_3} \int_0^{L_2} c_i(x_2,x_3;\Xi,t) dx_2 dx_3 \tag{12b}
\]

\[
\langle c_i^2(\Xi,t) \rangle^{1/2} = [(L_2L_3)^{-1} \int_0^{L_3} \int_0^{L_2} [c_i(x_2,x_3;\Xi,t)]^2 dx_2 dx_3]^{1/2} \tag{12c}
\]
smaller degree of uncertainty than are the point values. We would like to emphasize that the no-flow boundary condition at the vertical walls at $x_2 = 0$ and $x_2 = L_2$ (eqn (8)) and $x_3 = 0$ and $x_3 = L_3$ (eqn (8)) may affect the flow regime in the vicinity of these boundaries, and, concurrently, the spatial moments (11a), (11b) and (11c). A rigorous analysis of this effect, however, is beyond the limited scope of this technical note.

The change with elapsed time, $t$, in the normalized total mass of bromacil, $M/M_0$, where $M_0$ is the solute mass at $t = 0$, til a bromacil discharge has been started at the bottom of the flow domain ($x_1 = L_1$) is depicted in Fig. 2(a) and (b). The cumulative normalized degraded mass of bromacil, $M_d/M_0$, for the entire simulation period (251 days), is depicted in Fig. 2(c) and (d). As expected, because of degradation, the rate of decrease of $M$ with increasing $t$, decreases with increasing $t$. The dependence of the longitudinal, $R_1$, and transverse, $R_i$ ($i = 2,3$) components of the coordinate of the centroid of the solute plume, $\mathbf{R}$, upon the cumulative amount of applied water, $W$, is depicted in Fig. 2(e) and (f). As expected, the center of mass of bromacil is displaced vertically in the direction of the mean flow as $W$ increases, while the transverse components of $\mathbf{R}$, $R_2$ and $R_3$, remain essentially constant as $W$ changes. Although $R_1$ fluctuates slightly with $W$, overall, the rate of displacement, $dR_1/dW$, decreases with increasing $W$ (Fig. 2(g) and (h)). This stems from the unsteadiness and the compressibility of the unsaturated flow. The former is due to the cyclic recharge at the soil surface, while the latter is due to the spatial variability in water content and, concurrently, in the effective (water-filled) pore space available for flow.

Estimated values of the longitudinal, $S_{11}$, and transverse, $S_{ii}$ ($i = 2,3$) components of the spatial covariance tensor, $S_{ij}(t) = S_{ij}(t) - S_{ij}(0)$ ($i,j = 1,2,3$) as functions of the travel distance of the center of mass, $R_1$, are given in Fig. 2(i) and (j). The spatial covariance of the solute concentration distribution is a measure of the spreading of the distribution about its center of mass. Consequently, the changes in the

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**Fig. 2.** Scaled total mass ($M/M_0$) (a,b) and degraded mass ($M_d/M_0$) (c,d) of bromacil as functions of elapsed time, $t$; longitudinal ($R_1$) and transverse ($R_2$ and $R_3$) components of the coordinate location of the bromacil center of mass (e,f) and $dR_1/dW$ (g,h) as functions of cumulative amount of water, $W$; and longitudinal ($S_{11}$) and transverse ($S_{22}$ and $S_{33}$) components of the spatial covariance tensor ($i,j$) and the longitudinal component ($D_{11}$) of the macrodispersivity coefficient ($k,l$) as functions of $R_1$. Results are depicted for the CDE model (a,c,e,g,i,k) and the MIM model (b,d,f,h,j,l).
covariance structure with travel distance may reflect the changes of the concentration distribution that occur because of the heterogeneity induced in the solute velocity field by small-scale heterogeneity in both the physical and the chemical properties of the soil.

The longitudinal component, $S_{11}$, which fluctuates slightly with $R_1$, generally describes a transport process which is initially controlled by convection only (i.e. $S_{11}$ is initially proportional to the square of the travel distance) and which is then continuously changed to a convection-dispersion transport process (for which $S_{11}$ increases linearly with travel distance). This is demonstrated further by the longitudinal component of the effective macrodispersivity tensor, $D_{11} = (1/2)(dS_{11}/dR_1)$ depicted in Fig. 2(k) and (l). The fluctuations in $S_{11}$ and $D_{11}$ stem from the temporal variations in the flow conditions at the soil surface and are generally related to the fluctuations in $R_1$. The transverse components, $S_{22}$ and $S_{33}$, which also fluctuate with $R_1$, do not approach the constant asymptotic values which characterize the convection-dispersion transport process, when the mean head gradient coincides with the vertical (longitudinal) axis.

Compared with the CDE model, the MIM model suggests that the exchange of mass between the mobile and immobile regions retarded the bromacil degradation, slightly enhanced the displacement of the bromacil center of mass in the vertical direction at relatively short travel times, retarded it at longer travel times and slightly enhanced the bromacil spreading about its center of mass.

### 4.3 Solute breakthrough

With respect to groundwater contamination by chemicals moving through the unsaturated zone where risk assessment is required, an entity of interest is the solute BTC monitored at a horizontal CP located at an arbitrary vertical distance $\Xi$ from the soil surface. 

Mean BTCs in Fig. 3 in terms of the dimensionless variables, i.e. $T = R_1(t)/L$, $(C(T;\Xi) ≃ (c_f(T;\Xi)/c_i(T;\Xi))\mu T$, and $[(C(T;\Xi)/)^{1/2} = [(c_i(T;\Xi)/)^{1/2} / (c_f(T;\Xi))]^{1/2} / (c_f(T;\Xi))]^{1/2}$.

In general, the mean BTCs Fig. 3(a) and (b) exhibit skewness that is characterized by an earlier breakthrough, by an enhanced peak arrival, and by a longer tailing. The skewness of the mean BTCs, however, decreases with increasing distance to the CP. Compared to the CDE model, the MIM model exhibits unimodal pattern while the BTC standard deviation associated with the CDE model exhibits bimodal pattern. For a solute source of finite size, bimodal behavior may be due to the skewness of the one- and the two-particle travel time probability density functions (PDF)28. However, inasmuch as the BTC standard deviation at the shallower CP does not exhibit a clear bimodal pattern, it might be an artifact of only using a single realization of the parameters field.

Comparison of the BTCs in Fig. 3(a) and (b) and Fig. 3(c) and (d) suggests that the uncertainty in the expected BTCs,
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expressed as $CV = [\langle C(T;Z)^2 \rangle / \langle C(T;Z) \rangle] / \langle C(T;Z) \rangle$, is relatively large around the first arrival time, and decreases with increasing $T$, reaches a minimum in the vicinity of the $\langle C(T;Z) \rangle$ peaks, and increases with increasing $T$ as $T$ increases further, since $\langle C(T;Z) \rangle \to 0$ much faster than $[\langle C(T;Z)^2 \rangle ]^{1/2}$. Compared with the CDE model Fig. 3(a) and (c), the MIM model Fig. 3(b) and (d) suggests that the exchange of mass between the mobile and immobile regions of the soil increases the uncertainty in the predicted BTC.

The later finding has important implications regarding the assessment of groundwater contamination hazard. Due to the uncertainty in the predicted BTC, the assessment should be made in a probabilistic framework, i.e. by determining the probability distribution function of the accumulated mass, $M_a$, crossing the CP at a given vertical distance $Z$ from the injection zone, at time $t$. Assuming a plausible (e.g. lognormal) distribution for the PDF of the BTC across a CP located at $Z$, one can determine the probability of observing an accumulated mass, $M_a$, smaller than or equal to a critical value, $M_c$, crossing the CP at $Z$, at a given time $t$, i.e. $P(M_a \leq M_c; t, Z)$. For more details, see Russo. For example, for an amount of water equivalent to one (effective) pore volume that crossed the CP located at $Z = 0.71$ m (i.e. $T = R_s(t)/Z = 1$) and $M_a/M_c = 0.26$ and $0.13$ for the CDE and the MIM models, respectively. In other words, for given $Z$ and $T$, compared to a single region (CDE) model, the MIM model suggests that the exchange of mass between the mobile and immobile regions of the soil may considerably reduce the probability of observing an accumulated mass, $M_a \leq M_c$, crossing the CP located at $Z$.

4.4 Comparison with measured bromacil concentration profiles

The limited number of sampling depths and times precluded the characterization of the transport experiment of Tauber-Yasur et al. in terms of spatial or temporal moments of the bromacil concentration. Consequently, the present analysis is restricted to characterizing the measured bromacil concentration ($c^*$) profiles (expressed in terms of mass of bromacil per unit mass of soil) at a given elapsed time, $t$, in terms of horizontal averages, i.e. the mean, $< c^*(x; t) > = \Sigma c^*(x; t)/N_x$ and the standard deviation, $< c^*(x; t)^2 >^{1/2} = [\Sigma c^*(x; t)^2]/N_x$ and the standard deviation, $< c^*(x; t)^2 >^{1/2} = [\Sigma c^*(x; t)^2]/N_x$, where the subscripts $i(x_j)$ ($i = 1$ to $N_x$) and $j(x_k, x_l)$ ($j = 1$ to $N_x$) denote soil layer and profile, respectively, $N_x = 4, 5, 5$ and 6 for the four sampling dates, respectively, and $N_p = 20$. These averages, in turn, are compared with the horizontal averages of the simulated bromacil concentration, $c^*(x; t) = c(x,t)\theta(x,t)/\rho_s$, obtained from:

$$< c^*(x_1; t) > = (L_2L_3)^{-1} \int_0^{L_2} \int_0^{L_3} c^*(x_2, x_3; x_1, t) dx_2 dx_3$$

(13a)

$$< c^*(x_1; t)^2 >^{1/2} = (L_2L_3)^{-1} \int_0^{L_2} \int_0^{L_3} [c^*(x_2, x_3; x_1, t)]^2 dx_2 dx_3$$

(13b)

Means and standard deviations of measured and simulated bromacil concentration profiles corresponding to four different cumulative amounts of applied water are depicted in Fig. 3. This figure displays horizontal averages of the simulated concentration obtained by using the CDE model Fig. 4(a) and (c) and the MIM model Fig. 4(b) and (d). Mean values of both the measured and simulated $c^*$ profiles demonstrate the limitation of the downward movement of the bromacil by the relatively strong adsorption to the soil. On the first two sampling dates (at $t = 18$ days and $t = 32$ days), the agreement between the mean of the simulated

Fig. 4. Profiles of the means (a,b) and standard deviations (c,d) of the bromacil concentration, $c^*$, at four different elapsed times, $t$. Solid lines denote simulated profiles obtained from the CDE model (a,c) and the MIM model (b,d). The different symbols denote measured profiles.
$c^*$ profiles based on either the CDE model Fig. 4(a) or the MIM model Fig. 4(b) and the mean of the measured $c^*$ profiles was essentially the same. The mean $c^*$ profiles associated with the MIM model were slightly ahead of the measured mean $c^*$ profiles while the converse was true in the case of the CDE model. As more time elapses, however, the simulated mean $c^*$ profiles based on the CDE model, which vanish in the upper part of the soil, differ substantially from those based on the MIM model, which exhibit substantial values in the upper part of the soil, in relatively good agreement with the measured mean $c^*$ profiles. The latter profiles exhibit substantial skewness that, in turn, may be explained by the exchange of mass between the mobile and immobile regions of the soil and the transient, nonmonotonically characteristic of the flow. The fraction of the total water content which is stagnant, i.e. $\theta_m/\theta_m + \theta_im$, increases between successive water applications. Consequently, the total bromacil concentration in the top part of the soil profile may increase considerably during periods between successive water applications and it is not completely leached during infiltration periods. During the latter periods, for a given water flux at the soil surface, because $\theta_m/\theta_m + \theta_{im} < \theta$, the solute in the mobile region may travel faster than if the soil had contained only a single mobile region.

The profiles of the standard deviation of $c^*$ Fig. 4(c) and (d) generally follow the pattern of the mean $c^*$ profiles, with a peak at the same soil depth as that of the peak of the mean $c^*$ profile. As in the case of the mean $c^*$ profiles, on the first two sampling dates, the agreement between the standard deviation of the simulated $c^*$ profiles based on either the CDE model Fig. 4(c) or the MIM model Fig. 4(d) and that of the measured $c^*$ profiles is similar. As more time elapses the standard deviations of the simulated $c^*$ profiles based on the CDE model, which vanish in the upper part of the soil, differ substantially from those of the profiles based on the MIM model, which exhibit considerable values in the upper part of the soil, in relatively good agreement with the standard deviation of the measured $c^*$ profiles.

5 SUMMARY AND CONCLUSIONS

Field-scale transport of bromacil was analyzed by using two different model processes for local description of the transport. The first is the classical, one-region, convection-dispersion equation (CDE) model while the second is the two-region, mobile-immobile (MIM) model. The analyses were performed by means of detailed three-dimensional, numerical simulations of the flow and the transport employing field measurements of parameters of the local soil hydraulic properties, and laboratory measurements of the local solid/liquid partitioning coefficients and the first-order degradation rate coefficient. Results of these analyses, in terms of the means and the standard deviations of the simulated concentration profiles at different elapsed times, were compared with their measured counterparts obtained from a field-scale transport experiment conducted at the Bet Dagan site. The main results of the present investigation may be summarized as follows:

1. Both measured and simulated concentration profiles demonstrate the limitation of the downward movement of bromacil by its relatively strong adsorption to the soil.

2. For a given flow regime, mass exchange between the mobile and the immobile regions is shown to retard the bromacil degradation, to considerably affect the distribution of the bromacil resident concentration, $c$, at relatively large travel times, to affect slightly the spatial moments of the distribution of $c$, and to increase the skewing of the bromacil BTC and the uncertainty in its prediction, compared with the case in which the soil contained only a single (mobile) region.

3. At relatively short travel distances the agreement between the simulated mean and standard deviation concentration profiles based on either the CDE model or the MIM model and their measured counterparts is essentially the same. Unlike the MIM model, however, the CDE model failed to predict the highly skewed measured concentration profiles associated with longer travel distances or times.

Before concluding, we would like to stress that the three-dimensional simulation model did not involve any calibration or parameter estimation which employs the bromacil transport data. Instead, its input was based on independent field and laboratory measurements as well as on published data. We would like to emphasize, however, that the conclusions drawn from the present study should be considered with caution, inasmuch as the numerical results presented are subject to a few restrictions. One of the limitations arises from the lack of detailed field data on the spatial variability of the local partitioning coefficients and on the first-order degradation rate coefficient for bromacil in Bet Dagan soil. Another limitation stems from the fact that the expression eqn (5) for the local mass transfer rate coefficient was developed for idealized spherical aggregates of uniform size. The simplifying assumptions regarding the heterogeneity of the soil properties eqns (7a), (7b), (7c) and (7d), the local constitutive relationships for unsaturated flow (Gardner–Russo model, eqns (6a) and (6b)), the reactions that the solute may undergo (linear, equilibrium adsorption/desorption and first-order decay), the correlation scales (which are the same for the physical and the chemical properties of the soil), and the relationships between the physical and the chemical properties of the heterogeneous soil (negative cross-correlation between log $K_d$ and log $K_s$), also add to the limitations of the present investigation. With these limitations in mind, the main conclusion of this investigation is that the behavior of bromacil in the Bet Dagan field is quantified better when the transport on the local scale is modeled as a two-region, MIM model, than when a single-region, CDE model is used.
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