Sensitivity analysis of biodegradation of soil applied pesticides using a simulation model

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Abstract

Models, describing pesticide biodegradation in soil are necessary and useful tools. Shelton and Doherty [Soil Sci. Soc. Am. J. 61 (1997) 1085] proposed a model for describing rates of pesticide-substrate biodegradation in soil, which is relatively very simple. In this work, this model has been modified by incorporating the effect of toxicity of pesticides on microorganisms. It utilizes endogenous kinetics in the microorganism growth to include the effect of toxicity of pesticides, and considers Haldane kinetics instead of Monod kinetics for inhibitory pesticide substrate for predicting the biomass growth. Effects of change in variables on model predictions were studied. Further, the sensitivity of the biodegradation with respect to individual parameters and variables is also investigated. The sensitivity analysis identifies few parameters/variables, which are sensitive in some particular range of their values. It is also found that $K_s$ is insensitive to loss of efficacy ($\text{LE}_1$). In conjunction with the estimation of loss of efficacy, the model may be useful to suggest the choice of microorganisms depending on the values of its characteristic parameters.

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1. Introduction

The wide spread use of pesticides in agriculture resulted in the transfer of part of these chemicals into soil and ground water. The key processes by which the fate of chemicals is defined, are generally recognized as adsorption of the chemicals by the soil, volatilization of the chemicals from the soil, and its rate of degradation by biotic and abiotic mechanisms. Biodegradation is one of the most important ways to remove or to reduce pesticide concentration from soil, as complete removal is possible only by this process. This process is also important from the point of view of cost considerations. In this process introduction of cultured bacterial strains enhances microbial degradation.

Rifai et al. [1] described biodegradation as an effective process for contaminant attenuation in aquifers. Representing the reaction between oxygen and contaminant to be instantaneous, they developed the dual particle mover model by applying conservation principles to oxygen and contaminant only. Wu and Fan [2] developed a mathematical model for in situ biodegradation of contaminants in a soil bed. They considered that all the three substances, substrate, oxygen and biomass were involved in biodegradation. They found out the effect of insufficient oxygen supply, growth of microorganism and resistance to contaminant migration. Dhawan et al. [3] developed a contaminated aggregates bioremediation (CAB) model to analyze the bioremediation of soil and water in the aggregates. Shelton and Doherty [4] developed a very simple model for describing rates of pesticide-substrate biodegradation. They visualized the system as a four-compartment model and found out how loss of efficacy (\text{LE}_1) changes with different operational and constitutive parameters. However, in this model the effect of toxicity on microorganism has not been considered. The sensitivity analysis also has not been conducted, which helps to identify more sensitive parameters.

In this short communication, toxicity effects of microorganism in terms of endogenous metabolism of microbial biomass have been incorporated. Monod kinetics and Haldane kinetics [5] have been used simultaneously to represent microbial growth in the presence of non-inhibitory and inhibitory pesticides respectively, instead of Monod kinetics. Sensitivity analyses are carried out to identify significant operational and constitutive parameters.

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2. Simulation model

The biodegradation system has been described by a four-compartment model as done by Shelton and Doherty [4]. Fig. 1 shows the schematic representation of the four-compartment model. In deriving the model equations, following assumptions are made:

(i) Sorption to external soil surfaces and diffusion to internal soil particles are assumed to be first-order reversible transfer processes.

(ii) Complete mixing in every compartment, so that we can assume the volume of the each compartment as control volume in deriving model equations for each compartment.

(iii) Death kinetics is assumed to follow the following rate law, when Monod kinetics is used:

\[ \text{biomass death rate} = (k_d + k_i) S X \]

where \( k_d \) and \( k_i \) refer to the natural death, and death due to the toxicity, respectively [6].

(iv) Haldane kinetics is used for the microbial growth when inhibitory pesticide substrate is considered.

Model equations are as follows:

- For first compartment
  - Using Monod kinetics
    \[ \frac{dS}{dt} = -k_1 S + k_{-1} A - \frac{\mu_{\text{max}} SX}{(K_S + S)^2} \]  
    \[ \text{(1a)} \]
  - Using Haldane kinetics
    \[ \frac{dS}{dt} = -k_1 S + k_{-1} A - \frac{\mu_{\text{max}} SX}{(K_S + S + S^2/K_i)^2} \]  
    \[ \text{(1b)} \]

- For second compartment
  \[ \frac{dA}{dt} = k_1 S - (k_{-1} + k_2) A + k_{-2} U \]  
  \[ \text{(2)} \]

- For third compartment
  \[ \frac{dU}{dt} = k_2 A - k_{-2} U \]  
  \[ \text{(3)} \]

- For fourth compartment
  - Using Monod kinetics
    \[ \frac{dX}{dt} = \frac{\mu_{\text{max}} SX}{K_S + S} - (k_d + k_i) S X \]  
    \[ \text{(4a)} \]
  - Using Haldane kinetics
    \[ \frac{dX}{dt} = \frac{\mu_{\text{max}} SX}{K_S + S + S^2/K_i} \]  
    \[ \text{(4b)} \]

Model equations (1a), (2), (3) and (4a) with \( k_d = k_i = 0 \) reduce to the model, developed by Shelton and Doherty [4].

Model equations (1a), (2), (3) and (4a), and (1b), (2), (3) and (4b) represent predictive models, which consider the effect of toxicity in terms of death kinetics and Haldane kinetics, respectively. It is assumed that the pesticide concentration in solution, external soil surfaces and inside soil particles are in equilibrium. So initial conditions as given below can be used to solve the model equations:

\[ S_0 = 10 \, \mu g/ml, \quad A_0 = 10 \, \mu g/ml, \quad U_0 = 10 \, \mu g/ml \]

This is the situation when sorption and diffusion both are occurring.

3. Sensitivity analysis

Sensitivity analysis has been done on the basis of error estimation fundamentals [7].
The response variable \( E \) is a function of many variables:

\[
E = f(x_1, x_2, x_3, \ldots, x_n)
\]

where \( E \) is the response variable and \( x_1, x_2, x_3, \ldots, x_n \) are the parameters, those fixes the response variable. One obtains the following expression by expanding \( E \) by Taylor’s series and retaining only the first-order terms of series:

\[
\Delta E = \frac{\partial f}{\partial x_1} \Delta x_1 + \frac{\partial f}{\partial x_2} \Delta x_2 + \cdots + \frac{\partial f}{\partial x_n} \Delta x_n
\]

During these analyses only one variable can be varied at a time, keeping the other variables as constant. To find out the sensitivity of \( x_i \) on \( E \), all the variables are kept constant except \( x_i \). Sensitivity function \( \frac{\partial f}{\partial x_i} \), i.e. the slope of \( f \) with respect to \( x_i \), is calculated and plotted against \( x_i \) to find out the sensitivity with respect to \( x_i \).

Following this procedure the sensitivity with respect to each parameter and variable has been examined. Results of sensitivity analysis using the simulation model equations (1)-(4), have been discussed in Section 4. It is mentioned that in the discussion, figures, and tables, parameter has been used to indicate parameter or variable as the case may be.

### 4. Results and discussion

Model equations are solved using fourth-order Runge-Kutta method. A simulation program in C++ has also been developed. Clearly, there are an unlimited number of possible parameter combinations. However, based on the assumption that only pesticides in soil solution are available to control soil borne pests \([8]\), it is possible to define a threshold concentration below which there will be a hypothetical loss of efficacy \([4]\). For this purpose, the time required to reach a certain concentration for pesticide-substrate solution increases with the increase in death constants values. This effect is shown in Fig. 2. The relationship between \( LE_1 \) and decay constants (for \( k_d = k_t \)) has been shown in Fig. 3. This figure illustrates the general range of values of decay constants for microorganisms along with change in \( LE_1 \). This suggests that the constitutive and operational parameters on biodegradation process and on loss of efficacy have been discussed in the following sub sections. Model predictions without Haldane kinetics or death kinetics remain consistent as expected with the results given by Shelton and Doherty \([4]\).

#### 4.1. Effect of death constant

The growth and death of microorganisms, should be considered simultaneously. Time required to reach a certain concentration for pesticide-substrate solution increases with the increase in death constants values. This effect is shown in Fig. 2. The relationship between \( LE_1 \) and decay constants (for \( k_d = k_t \)) has been shown in Fig. 3. This figure illustrates the general range of values of decay constants for microorganisms along with change in \( LE_1 \). This suggests that the
microorganisms having lower values of $k_d$ and $k_t$ should be chosen.

4.2. Effect of inhibition constant

When we consider the Haldane kinetics for microbial growth rate, inhibition constant becomes an important parameter, which affects the substrate depletion rate. Fig. 4 illustrates that the time required for pesticide substrate to reach a particular concentration increases with the decrease in inhibition constant. This is consistent with the Haldane kinetics. Lower values of inhibition constant represent greater product inhibition, which causes a decrease in microbial growth rate, i.e. for the biodegradation, less biomass is available. So time required to reduce soil solution concentration is higher. A geometric relationship is observed between $LE_1$
and inhibition constant ($K_i$) from Fig. 5. This figure shows that $\text{LE}_1$ decreases rapidly when $K_i$ value increases from 1 to 10 $\mu$g/ml. For $K_i$ value between 10 and 100 $\mu$g/ml the decrease in $\text{LE}_1$ is very less.

### 4.3 Sensitivity analysis

In order to identify sensitive parameters with respect to loss of efficacy normalized slope is plotted against the value of normalized parameters in Figs. 6 and 7. Normalization has been done so that different partial derivatives may be plotted on the same plot. In this regard Table 1 provides the minimum and maximum values of a parameter, and corresponding values of slopes, i.e., partial derivatives, whereas Table 2 gives the expressions used for normalization of slopes and parameters as discussed above. The effect of change in various parameters is described as follows:

From the critical examination of Figs. 6 and 7, it is concluded that

(i) Loss of efficacy is sensitive to $\mu_{\text{max}}$ for normalized parameter less than 0.33.
(ii) Loss of efficacy is sensitive to $K_s$ for normalized parameter less than 0.1.
(iii) Loss of efficacy is sensitive to $X_0$ for normalized parameter less than 0.1.
(iv) Loss of efficacy is sensitive to $k_d$ for normalized parameter greater than 0.6.

However, loss of efficacy is insensitive to changes in half saturation growth constant ($K_s$). For initial pesticide concentration ($S_0$) normalized slope first increases up to 0.4, it becomes constant from 0.4 to 0.8, and then again start to increase. For the effect of $S_0$ it may be said that increase in $S_0$ effects the $\text{LE}_1$ as expected.

Table 3 has been prepared by using Figs. 6 and 7, and Table 2. This table provides at a glance range of values of various parameters to which $\text{LE}_1$ is sensitive.
Fig. 7. Plots of slope \( (\equiv \Delta \text{LE}_1/\Delta x_i) \) with the parameter \( x_i \) (for normalization, refer Table 2).

**Table 1**

Minimum and maximum values taken for parameters and corresponding slopes

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Parameter value used in simulation</th>
<th>Slope of LE₁ vs. parameter curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_d ) (h⁻¹)</td>
<td>0, 0.004</td>
<td>−3450, 572350</td>
</tr>
<tr>
<td>( K_i ) (µg/ml)</td>
<td>1, 100</td>
<td>−232.482, 218076.6</td>
</tr>
<tr>
<td>( K_s ) (µg/ml)</td>
<td>0, 100</td>
<td>9.786, 12.726</td>
</tr>
<tr>
<td>( \mu_{\text{max}} ) (h⁻¹)</td>
<td>0.02, 0.2</td>
<td>−200762, −1984.18</td>
</tr>
<tr>
<td>( S_0 ) (µg/ml)</td>
<td>2, 40</td>
<td>9.8282, 88.9274</td>
</tr>
<tr>
<td>( X_0 ) (µg/ml)</td>
<td>( 1.0 \times 10^{-6} )</td>
<td>9.8282, 21.8</td>
</tr>
</tbody>
</table>

**Table 2**

Normalization of parameters and slopes

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Normalized parameter = parameter ( (\text{maximum} - \text{minimum}) ) / value of parameter</th>
<th>Normalized slope = slope ( (\text{maximum} - \text{minimum}) ) / value of slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_d )</td>
<td>( 0 )</td>
<td>( 0.004 )</td>
</tr>
<tr>
<td>( K_i )</td>
<td>( K_i )</td>
<td>( 100 )</td>
</tr>
<tr>
<td>( \mu_{\text{max}} )</td>
<td>( \mu_{\text{max}} )</td>
<td>( 0.02 )</td>
</tr>
<tr>
<td>( S_0 )</td>
<td>( S_0 )</td>
<td>( 40 )</td>
</tr>
<tr>
<td>( X_0 )</td>
<td>( X_0 )</td>
<td>( 10 )</td>
</tr>
</tbody>
</table>
Table 3  
Parameters and their range of sensitivity (range has been calculated from Figs. 6 and 7, and Table 2)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range, where the parameter is sensitive</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_d$ (h$^{-1}$)</td>
<td>$&gt;2.4 \times 10^{-3}$</td>
</tr>
<tr>
<td>$K_i$ (µg/ml)</td>
<td>&lt;10</td>
</tr>
<tr>
<td>$\mu_{max}$ (h$^{-1}$)</td>
<td>&lt;0.06</td>
</tr>
<tr>
<td>$S_0$ (g/µg/ml)</td>
<td>LE increases with the increase in $S_0$</td>
</tr>
<tr>
<td>$X_0$ (g/µg/ml)</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

5. Conclusions

In the present work, model of Shelton and Doherty [4] has been modified by incorporating the toxicity effects of pesticides on microorganisms. Monod kinetics with endogenous kinetics and Haldane kinetics are simultaneously used to represent the microbial growth rate for non-inhibitory and inhibitory pesticides, respectively. This model can be used to predict biodegradation rates, and loss of efficacy if pest toxicological data are available, and to conduct simulation and sensitivity analysis.

Simulations have been conducted to examine the effects of microbial growth constants, initial pesticide substrates and biomass concentrations on the time required for the loss of efficacy. Besides, sensitivity analyses have been carried out to identify the important parameters.

Sensitivity analysis identifies the range of constitutive and operational parameters, to which the LE$_1$ is sensitive. Except $K_s$, all the parameters are sensitive in some particular range. Microorganisms (mixed cultures) having higher $\mu_{max}$ value, lower $K_i$ value and higher $K_i$ value are always the better choice. These observations may be used for designing pest control strategies using biodegradable pesticides and to decide the initial pesticide concentration, initial biomass concentration and choice of microorganisms.

Acknowledgements

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References