Predicting Pesticide Biphasic Soil Concentration Decline Under Field Conditions: Model-Data Comparison

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Outline

- Introduction
- Model development
- Model evaluation and field studies
- Simulation results
- Conclusions
Introduction

• Biphasic degradation patterns of pesticides with initial fast decline followed by slower degradation phase are often observed
• Current pesticide regulatory modeling tools like Pesticide Root Zone Model (PRZM) do not handle biphasic degradation
• Forces Single First Order (SFO) degradation kinetics to represent the actual biphasic degradation characteristics in simulation
• Need to incorporate Double First-Order in Parallel (DFOP) kinetics model into a PRZM-based environmental fate model to account for biphasic degradation
Model Development

• synPRZM developed to treat the chemical under simulation as two separate fractions, each with its own distinct degradation rate
• Both fractions are simulated simultaneously each day, and the sum of their results is output as a whole for the chemical
• DFOP parameters can be derived from laboratory soil metabolism studies using kinetics calculation programs
• Each fraction has linear/nonlinear and/or time-dependent sorption, temperature/moisture-dependent degradation, and other fate processes.
Model Evaluation

• Model evaluation was carried out by using independently measured laboratory parameters to predict field dissipation study data from 21 geographical locations in the US.
• Biphasic kinetics parameters were obtained from four laboratory soil metabolism studies independent of field dissipation studies.
• Linear equilibrium soil sorption parameter (Koc): 113 mL/g (average from 28 soils)
• Degradation of each fraction was dependent on soil temperature (Q10=2) and moisture (correction factor 0.7)
• Site-specific soil, weather and irrigation data were used.
Calculated Biphasic Degradation Rates

- **DFOP equation**
  \[ C_t = C_0 g^{-k_1 t} + C_0 (1 - g)^{-k_2 t} \]
  - \( g \) is the fraction of the \( C_0 \) as being Fraction 1
  - \( k_1 \) = rate constant for Fraction 1 in 1/days
  - \( k_2 \) = rate constant for Fraction 2 in 1/days
- **NAFTA kinetics calculation (PestDF) by using available laboratory soil metabolism studies**
- **DFOP fits provided the fraction of the initial chemical that degrades at the fast rate**

Example of a kinetics calculation output

Average results from four different soil metabolism studies

<table>
<thead>
<tr>
<th>Fraction</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>g</td>
<td>0.51175 k1</td>
</tr>
<tr>
<td>1-g</td>
<td>0.48825 k2</td>
</tr>
</tbody>
</table>
Field Study Sites

- Field dissipation study sites (21) for the test substance selected covering multiple regions
## Soil Characteristics at Field Study Sites

<table>
<thead>
<tr>
<th>Sites</th>
<th>pH</th>
<th>OM</th>
<th>%Sand</th>
<th>%Silt</th>
<th>%Clay</th>
<th>Classification</th>
<th>Study period</th>
</tr>
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<tbody>
<tr>
<td>Monmouth, IL</td>
<td>5.5</td>
<td>4.4</td>
<td>8.9</td>
<td>67.1</td>
<td>24.0</td>
<td>silt loam</td>
<td>1994-1999</td>
</tr>
<tr>
<td>Brimfield, IL</td>
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<td>4.9</td>
<td>3.9</td>
<td>58.1</td>
<td>38.0</td>
<td>silty clay loam</td>
<td>1994-1999</td>
</tr>
<tr>
<td>St Joseph, IL</td>
<td>5.7</td>
<td>3.7</td>
<td>12.0</td>
<td>56.0</td>
<td>32.0</td>
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<td>1994-1999</td>
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<tr>
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<td>5.5</td>
<td>4.8</td>
<td>57.2</td>
<td>32.0</td>
<td>silty clay loam</td>
<td>1994-1999</td>
</tr>
<tr>
<td>Odell, IL</td>
<td>6.6</td>
<td>4.8</td>
<td>11.5</td>
<td>52.5</td>
<td>36.0</td>
<td>silty clay loam</td>
<td>1994-1999</td>
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<tr>
<td>Boone, IA</td>
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<td>7.0</td>
<td>31.0</td>
<td>45.0</td>
<td>24.0</td>
<td>loam</td>
<td>1994-1999</td>
</tr>
<tr>
<td>Lyle, MN</td>
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<td>2.4</td>
<td>28.3</td>
<td>48.2</td>
<td>23.5</td>
<td>loam</td>
<td>1994-1999</td>
</tr>
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<td>Desoto, KS</td>
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<td>3.4</td>
<td>10.8</td>
<td>59.2</td>
<td>30.0</td>
<td>silty clay loam</td>
<td>1994-1999</td>
</tr>
<tr>
<td>Oregon, MO</td>
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<td>3.4</td>
<td>10.8</td>
<td>59.2</td>
<td>30.0</td>
<td>silty clay loam</td>
<td>1994-1999</td>
</tr>
<tr>
<td>St Peter, MN</td>
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<td>5.2</td>
<td>31.5</td>
<td>38.5</td>
<td>30.0</td>
<td>clay loam</td>
<td>1994-1999</td>
</tr>
<tr>
<td>Fairmont, NE</td>
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<td>3.2</td>
<td>14.2</td>
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<td>32.0</td>
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<td>1994-1999</td>
</tr>
<tr>
<td>Elkhorn, WI</td>
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<td>3.0</td>
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<td>68.0</td>
<td>24.0</td>
<td>silt loam</td>
<td>1994-1999</td>
</tr>
<tr>
<td>Plainview, TX</td>
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<td>1.1</td>
<td>47.4</td>
<td>23.4</td>
<td>29.2</td>
<td>sand clay loam</td>
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<td>Vicksburg, MS</td>
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<td>1.0</td>
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<td>14.0</td>
<td>silt loam</td>
<td>1986-1987</td>
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<td>Goldsboro, NC</td>
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<td>1.3</td>
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<td>6.0</td>
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<td>3.4</td>
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<td>silt clay loam</td>
<td>1986-1987</td>
</tr>
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<td>2.3</td>
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<td>68.9</td>
<td>24.2</td>
<td>silt loam</td>
<td>1995-2000</td>
</tr>
<tr>
<td>Doran, MN</td>
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<td>5.6</td>
<td>40.3</td>
<td>22.6</td>
<td>37.1</td>
<td>clay loam</td>
<td>1995-2000</td>
</tr>
<tr>
<td>Watertown, SD</td>
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<td>5.77</td>
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<td>47.9</td>
<td>29.1</td>
<td>clay loam</td>
<td>1995-2000</td>
</tr>
<tr>
<td>Ithaca, NY</td>
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<td>6.2</td>
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<td>54.0</td>
<td>35.0</td>
<td>silty clay loam</td>
<td>2000-2002</td>
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<tr>
<td>Knoxville, TN</td>
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<td>1.9</td>
<td>36.0</td>
<td>44.0</td>
<td>20.0</td>
<td>fine loamy</td>
<td>2010-2012</td>
</tr>
</tbody>
</table>
Soil Temperature and Moisture Adjustment

- Without soil temperature and moisture corrections, the model tends to under-predict slow degradation phase.
- Inclusion of soil temperature and moisture corrections can greatly improve model performance, especially raising the tails of the slow degradation process.

![Total soil concentration (0-15 cm) St Peter, MN Plot 2](chart1)

![Total soil concentration (0-15 cm) St Peter, MN Plot 3](chart2)
Simulation Results

**Moumonth, IL**

**St Peter, MN**

**Fairmont, NE**
Simulation Results (Continued)

**Brimfield, IL**

**St Joseph, IL**

**Gibson City, IL**

**Odell, IL**

**Boone, IA**

**Oregon, MO**
Simulation Results (Continued)

Desoto, KS

Total soil concentration (0-15 cm) Desoto, KS
Plot 2

Lyle, MN

Total soil concentration (0-15 cm) Lyle, MN
Plot 2

Elkhorn, WI

Total soil concentration (0-15 cm) Elkhorn, WI
Plot 2

Ashley, IL

Total soil concentration (0-15 cm) Ashley, IL
Plot 2

Doran, MN

Total soil concentration (0-15 cm) Doran, MN
Plot 2

Watertown, SD

Total soil concentration (0-15 cm) Watertown, SD
Plot 2
Simulation Results (Continued)

Vicksburg, MS

Total soil concentration (0-5 cm) Vicksburg, MS

Champaign, IL

Total soil concentration (0-5 cm) Champaign, IL

Ithaca, NY

2001 total soil concentration (0-10 cm) NY EPOST

Goldsboro, NC

Total soil concentration (0-5 cm) Goldsboro, NC

Plainview, TX

Total soil concentration (0-15 cm) 23-TX-97-816 Plot 4

Knoxville, TN

2012 total soil concentration (0-8 cm) TN
Conclusions

• DFOP was successfully implemented in synPRZM, thus enabling accurate simulation of biphasic degradation profiles. The model is flexible to incorporate other fate processes and the impact of soil temperature and moisture.

• Using DFOP parameters obtained from independently measured laboratory studies, synPRZM predicted field measurements over 21 geographical locations reasonably well without elaborate model calibration.

• Model also predicted soil pore water concentrations reasonably well (see Chen et al. presentation AGRO328).
Thank You