A Mass Balance Approach Updating the SWAT Pesticide Module for Applications to EMCONs

K. BRASSETT AND L.J. THIBODEAUX
Cain Department Chemical Engineering, Louisiana State University, Baton Rouge, LA USA
kbrass2@gmail.com;thibod@lsu.edu

Platform presentation at 2011 SWAT, University of Castilla La Mancha, Toledo, SPAIN. June 15-17, 2011.
Objective

• Updating pesticide model in SWAT

• Rederive the Lavoisier mass balance in the pesticide component of SWAT

• Run numerical simulations comparing the current pesticide model in SWAT and the newly developed Lavoisier mass balance model
Significance of SWAT

- Predict long-term impact of management practices on basin
- Chemical fate in surface and ground waters
- Increasing importance with increase in herbicides, pesticides & EMCON’s

- Examples used
  - Herbicide: Monsanto’s Round Up (glyphosate)
  - EMCON (Growth Hormone): trenbolone
  - Pesticides: malathion, methoxychlor, DiBrClpropane
Modeling based on Hydraulic Response Unit (HRU) [SWAT Theoretical Documentation, 2005]

- Similar Soil types

- HRU- lumped land areas within the sub-basin with unique land cover, soil, management combinations [SWAT Theoretical Documentation 2005].

- Control Volume for chemical fate model
3 SWAT Processes
1. Combined 1\textsuperscript{st} order rate constant
2. Combined 1\textsuperscript{st} order rate constant
3. Constant rate parameter
SWAT Soil Surface Pesticide Algorithm

1. $P_{st} = P_{sto} e^{-(K_{rxn})t}$
   - Evaporation
   - Degradation

2. $P_{st} = P_{sto} e^{-(K_{sol})t}$
   - Soluble Runoff
   - Lateral Runoff
   - Leaching

3. $P_{st} = P_{sto} - tK_{ero}$
   - Sediment Runoff

*Sequence is not fixed

<table>
<thead>
<tr>
<th>Variable</th>
<th>Definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{st}$</td>
<td>Pesticide remaining in layer at time t</td>
<td>kg/ha</td>
</tr>
<tr>
<td>$P_{sto}$</td>
<td>Initial pesticide concentration loading</td>
<td>kg/ha</td>
</tr>
<tr>
<td>$K_{rxn}$</td>
<td>Rate constant for degradation, evaporation and removal of pesticide in soil</td>
<td>1/day</td>
</tr>
<tr>
<td>$K_{ero}$</td>
<td>Constant rate of Pesticide sorbed into lateral runoff</td>
<td>kg/ha*day</td>
</tr>
<tr>
<td>$K_{sol}$</td>
<td>Rate constant for soluble transport in runoff</td>
<td>1/day</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
<td>day</td>
</tr>
</tbody>
</table>
SWAT

- Computation procedure within SWAT is performed sequentially since there are three equations.

LAVOISIER MASS BALANCE

- The computation algorithm is a single equation reflecting the overall processes which occur simultaneous.
Lavoisier Mass Balance (LVM)

- Mass Balance on 1cm soil surface layer
  - Simultaneous Vs. sequencing in SWAT
- Integrated Mass Balance for comparison

\[
P_{st} = \left[ P_{sto} - \frac{K_{ero}}{K} \right] e^{-(Kt)} + \frac{K_{ero}}{K}
\]

where: \( K = (K_{evap} + K_{rxn} + K_{sol}) \)

; \( K_{rxn} = K_{bio} + K_{photo} + K_{hyd} \)

- Evaluated using glyphosate, trendbolone, methoxychlor, melathion, dibromochloropropane
## Model Parameters

<table>
<thead>
<tr>
<th>Chemical</th>
<th>$t_{1/2}$[d]</th>
<th>Koc [m$^3$/kg]</th>
<th>Hp</th>
<th>MW</th>
<th>$K_{rxn}$ [d$^{-1}$]</th>
<th>$K_{evap}$ [d$^{-1}$]</th>
<th>$K_{sol}$ [d$^{-1}$]</th>
<th>$K_{ero}$ [mgA/d*m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glyphosate</td>
<td>2</td>
<td>2.072</td>
<td>5.76E-9</td>
<td>169</td>
<td>0.3465</td>
<td>5.37E-9</td>
<td>4.17E-4</td>
<td>0.444</td>
</tr>
<tr>
<td>Glyphosate</td>
<td>197</td>
<td>2.072</td>
<td>5.76E-9</td>
<td>169</td>
<td>0.0035</td>
<td>5.37E-9</td>
<td>5.37E-9</td>
<td>0.444</td>
</tr>
<tr>
<td>Trenbolone</td>
<td>4</td>
<td>0.589</td>
<td>7.77E-8</td>
<td>270</td>
<td>0.173</td>
<td>2.53E-3</td>
<td>1.05E-3</td>
<td>4.44E-5</td>
</tr>
<tr>
<td>DiBrClpropane</td>
<td>45</td>
<td>0.04</td>
<td>1.0E-2</td>
<td>202</td>
<td>0.015</td>
<td>3.78</td>
<td>9.35E-2</td>
<td>0.444</td>
</tr>
<tr>
<td>Malathion</td>
<td>1</td>
<td>0.23</td>
<td>4.9E-6</td>
<td>330</td>
<td>0.693</td>
<td>2.64E-4</td>
<td>1.83E-2</td>
<td>0.444</td>
</tr>
<tr>
<td>Methoxychlor</td>
<td>100,360</td>
<td>80</td>
<td>3.0E-5</td>
<td>346</td>
<td>0.00693</td>
<td>4.56E-6</td>
<td>5.40E-5</td>
<td>0.444</td>
</tr>
</tbody>
</table>
**SWAT Sequencing**

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1→2→3</td>
<td>1→3→2</td>
<td>2→3→1</td>
<td>3→1→2</td>
<td>2→1→3</td>
<td>3→2→1</td>
</tr>
</tbody>
</table>

1) Reaction
2) Solute Transport
3) Pesticide in Runoff
Results: Glyphosate

Glyphosate ($t_{1/2} = 2d$)

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1→2→3</td>
<td>1→3→2</td>
<td>2→3→1</td>
<td>3→1→2</td>
<td>2→1→3</td>
<td>3→2→1</td>
</tr>
</tbody>
</table>

1) Reaction; 2) Solute Transport; 3) Pesticide in Runoff
Results: Glyphosate

Glyphosate (t_{1/2}=197d)

- Mass Balance
  - A
  - B
  - C
  - D
  - E
  - F

- % Difference Mass Balance

- Pesticide Remaining [kg/ha] vs. Time [days]

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td>1</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

1) Reaction; 2) Solute Transport; 3) Pesticide in Runoff

6/15/2011
Results: Trenbolone

![Graph showing the remaining pesticide over time and mass balance for Trenbolone.](image)

### Mass Balance

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1→2→3</td>
<td>1→3→2</td>
<td>2→3→1</td>
<td>3→1→2</td>
<td>2→1→3</td>
<td>3→2→1</td>
</tr>
</tbody>
</table>

1) Reaction; 2) Solute Transport; 3) Pesticide in Runoff
Results

% Difference Mass Balance

Dibromochloropropane

Malathion

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1→2→3</td>
<td>1→3→2</td>
<td>2→3→1</td>
<td>3→1→2</td>
<td>2→1→3</td>
<td>3→2→1</td>
</tr>
</tbody>
</table>

1) Reaction; 2) Solute Transport; 3) Pesticide in Runoff
Results Continued

![Graph showing the % difference in mass balance over time for different samples labeled A through F. Each line represents a different sample and shows a downward trend as time increases, indicating a decrease in mass balance. The x-axis represents time in days, ranging from 0 to 200, and the y-axis represents the % difference in mass balance.]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction Sequence</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1→2→3</td>
</tr>
<tr>
<td>B</td>
<td>1→3→2</td>
</tr>
<tr>
<td>C</td>
<td>2→3→1</td>
</tr>
<tr>
<td>D</td>
<td>3→1→2</td>
</tr>
<tr>
<td>E</td>
<td>2→1→3</td>
</tr>
<tr>
<td>F</td>
<td>3→2→1</td>
</tr>
</tbody>
</table>

1) Reaction; 2) Solute Transport; 3) Pesticide in Runoff
Conclusion

• The present SWAT pesticide module is the appropriate place for developing an EMCON module
• Transforming the sequential process code to a simultaneous process code that reflects the[Lavoisier] mass balance on the HRU is recommended
• Further research EMCON reaction, transport and thermodynamic partitioning and update pesticide algorithms
• Extend application of mass balance approach to deeper soil layers and other sub-units on the HRU
Questions?
SWAT Model
Assumptions/Characteristics

- User defined Watershed divided into 2-5 sub layers
- Chemical concentration and properties assumed constant in control volume (HRU)
- Model time series
  - 1 time step = 1 day
  - Growing seasons
- Rain, temperature, water content, concentration in layers, etc. updated daily
- Model tracks chemodynamics in HRU
- Model computes the mass of chemical, soil in runoff from HRU
The evaporation half life ($\tau_{1/2}$) is the ratio of the overall mass transfer coefficient for pesticide vapor transport from the soil-to-atmosphere (to the soil-to-air pesticide partition coefficient ($K_{A13}$), soil thickness ($h_3$), and bulk density of the soil ($\rho_3$)). The units respectively are day$^{-1}$, meters/day, m$^3$/kg, meters, and kg/m$^3$.

The overall mass transport coefficient, depends on the air side mass transfer coefficient ($k_{A1}$), the chemical's molecular diffusivity in air ($D_{A1}$), the volumetric air content of the soil ($\epsilon_1$), and the soil thickness.
Round UP

• Active ingredient - glyphosate
• “inert” ingredients - Ethoxylated tallowamine, isopropylamine, Diazinon
• Leading herbicide
  • 100 million pounds applied to U.S farms and lawns every year (EPA)
• Regulated at relatively high concentrations in our drinking water
  • Toxic
  • Carcinogenic
• Roundup’s “inert” ingredients have been recently seen to have toxic effects on human cells

EMCONS, PBT, & Emerging Toxic substances

- endocrine disrupting compounds (EDCs)
- pharmaceutical drugs
- personal care products (PPCPs)
- atrazine (herbicide)
- caffeine
- Contamination of drinking water
Development of Lavoisier Mass Balance

\[
\frac{d}{dt} \iiint_V C_A dV = \iiint_A C_A \mathbf{V} \cdot (-\mathbf{n}) dA + \iiint_A (\mathbf{j}_D + \mathbf{j}_V) \cdot (-\mathbf{n}) dA + \iiint_V r_A dV + \sum_{1}^{n} w_A
\]

<table>
<thead>
<tr>
<th>Accumulation</th>
<th>Adveactive Transport</th>
<th>Diffusive Transport</th>
<th>Chemical Reaction</th>
<th>Forced Inputs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle(soils) erosion</td>
<td>Evaporation</td>
<td></td>
<td></td>
<td>Pesticides</td>
</tr>
<tr>
<td>Solubility</td>
<td>Leaching</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 0.3: Schematic representation of the hydrologic cycle.

[Swat Theoretical Documentation, 2005]
Mass Balance continued – connecting the media boxes

Chemical flux across media boxes, examples:

Vaporization from soil to air:

\[ j_D = k_a |C_A^* - C_A(\text{air})| \]

Soil particle erosion to atmosphere:

\[ j_V = \nu_r C_A(\text{soil surface}) \]

Soil-to-air partitioning:

\[ C_A(\text{soil}) = K_{SA} \cdot C_A^* \]

Air-to-water partitioning:

\[ C_A(\text{air}) = H_C \cdot C_A(\text{water}) \]

Transport coefficients \( k_a \) and \( \nu_r \) (m s\(^{-1}\)); partition coefficients \( K_{SA} \) and \( H_C \) (L kg\(^{-1}\)).