Experimental determination of Plant uptake factors (PUFs) for three different crops as a function of logK_{ow} and pH in a hydroponic like test system under greenhouse conditions

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Introduction

The uptake of plant protection products and their degradation products by plants is a relevant dissipation process that limits their availability for leaching, run-off and volatilisation in addition to processes like soil adsorption or degradation. Chemical hydrophobicity (logK_{ow}) and additionally for ionisable compounds the acid dissociation constant (pK_{a}) are the most important chemical properties determining the ratio between a compound’s concentration in the plant-root system to that in the pore water around the roots. All pesticide leaching models used in European ground water risk assessment use the same following equation for estimating the amount of substance taken up by plants:

\[
\frac{dm_{\text{uptake}}}{dt} = Q_{\text{transpiration}} \times PUF \times C_{\text{soil-water}}
\]

The plant uptake factor (PUF) contributes to the mass balance at a given time and space in the soil; any plant uptake in principle leads to a decrease of compound mass in the surrounding soil system. Recommendations on parameter selection are given by the FOCUS groundwater working group (FOCUS 2003). The TSCF (transpiration stream concentration factor) is used as a surrogate and the Briggs equation is recommended to derive TSCF values that are then used as PUF values. Otherwise, TSCF values of 0.5 for systemic, non-ionic substances and 0 for all others are recommended.

A test system accepted by authorities to determine PUF values is currently lacking. The purpose of this study was to validate an experimental protocol that allows for accurate determination of the PUF to be used in pesticide fate modelling. PUF values of eight different substances were determined using a hydroponic-like test system, where plants were kept with their root systems in a simulated soil pore water consisting of a buffered 0.01 M CaCl_{2} solution spiked with the single test items. The eight substances were selected to cover a range of lipophilicity (logK_{ow} from 0.15 to 3.9). For each substance, the experiment was conducted with three different plant species (wheat, oilseed rape, tomato) under three pH conditions (pH 5.5, 6.5 and 7.5), respectively.

Theory

As the concentration in soil pore water is the result of sorption and degradation processes, (considered separately in models), the test system was chosen to be a simplified representation of the soil pore water, where these other processes were omitted. The variation of the compound concentration in the test solution was therefore only a result of the plant uptake. The PUF was determined with the following equation 2.

\[
PUF = \ln \left( \frac{m_{\text{solution_fin}}}{m_{\text{solution_init}}} \right) / \ln \left( \frac{V_{\text{solution_fin}}}{V_{\text{solution_init}}} \right)
\]

m_{solution_init} & m_{solution_fin}: mass of test item in solution on initial day (0) and final day (8)
V_{solution_init} & V_{solution_fin}: mass of test item in solution on initial day (0) and final day (8)
Material and methods

The test system used in this study were 1-L brown glass vessels in which the plants without soil (pre-grown in soil for 5-6 weeks) are inserted into the test solution and cultivated for 8 days under controlled greenhouse conditions. For each substance, the experiment was conducted with three different plant species (Wheat, Oil seed rape, Tomato) and at three pH-level by using biological buffers (5.5, 6.5 and 7.5). By determining the volume uptake and concentration at the start and end of the incubation period the PUFs were calculated by using Equation 1. The experiments were performed with eight test items within pesticides, metabolites or other environmentally interesting compounds (cf. Table 1) which were chosen to cover a broad range of properties (dissociating or not, lipophilicity), and selected to be hydrolytically stable and non-phytotoxic under test conditions.

Table 1. Properties of the test items

<table>
<thead>
<tr>
<th>Test items</th>
<th>Concentration ([µg,L^{-1}])</th>
<th>(K_{oc}) ([ml,g^{-1}])</th>
<th>(pK_a)</th>
<th>(\log K_{ow})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>77.5</td>
<td>&gt;1000</td>
<td>2.7, 5.1</td>
<td>0.16</td>
</tr>
<tr>
<td>B</td>
<td>67.0</td>
<td>1000</td>
<td>2.3</td>
<td>3.9</td>
</tr>
<tr>
<td>C</td>
<td>77.6</td>
<td>736</td>
<td>3.94</td>
<td>-0.4 @ pH 2.2, 0.32 @ pH 7</td>
</tr>
<tr>
<td>D</td>
<td>55.1</td>
<td>&lt;10</td>
<td>3.3(^c)</td>
<td>0.6</td>
</tr>
<tr>
<td>E</td>
<td>78.3</td>
<td>&lt;10</td>
<td>&lt;4(^c)</td>
<td>0.8</td>
</tr>
<tr>
<td>F</td>
<td>75.7</td>
<td>700-800</td>
<td>4.2</td>
<td>2.2</td>
</tr>
<tr>
<td>G</td>
<td>75.0</td>
<td>400</td>
<td></td>
<td>2.2</td>
</tr>
<tr>
<td>H</td>
<td>71.0</td>
<td>10-50</td>
<td>4.2</td>
<td>2.7 @ pH 4, 0.15 @ pH 7</td>
</tr>
</tbody>
</table>

\(^a\) in solution on application, \(^b\) organic carbon coefficient, \(^c\) calculated, \(^d\) non-dissociating

Results

The test system was found valid regarding mass balance, stability in solution, side processes (glass adsorption, volatilisation, evaporation) and plant health. Independent of crop type, neither hydrophobicity nor pH of the test solution showed a great influence on the PUF. The mean PUFs calculated over all test items (with the exception of test item A), crop types and pH values ranged from 0.62 to 1.64, with an arithmetic mean of 1.01 (cf. Figure 1).

Figure 1. Arithmetic mean plant uptake factor [PUF] (±SD, over pH levels and replicates) as a function of \(\log K_{ow}\) for each crop type

Conclusions

The experimentally derived PUF values covering a \(\log K_{ow}\) range from 0.15 to 3.9, pH range from 5.5 to 7.5 and three different crops did not indicate any overestimation of the plant uptake if 0.5 will be used as default value for substances with pH-independent properties. Furthermore the presented test system is suitable to determine crop-, pH- and compound-specific PUFs for a refined pesticide leaching modelling.

References