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

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**Introduction**

Pesticides and their metabolites are taken up from the soil pore water by the plants with the transpiration stream.

This process limit their availability for subsequent distribution in adjacent environmental compartments!
PUF as soil water depletion factor -> Relevant input parameter in all FOCUS groundwater models

- **PUF = 1**
- **PUF < 1**
- **PUF = 0**
## Recommendations PUF parameterization

<table>
<thead>
<tr>
<th>FOCUS EU&lt;sup&gt;1)&lt;/sup&gt;</th>
<th>German Approach&lt;sup&gt;2)&lt;/sup&gt;</th>
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</thead>
</table>
| • Default PUF 0.5 for systemic substances and 0 else
  • Use estimated TSCF as surrogate with reference to “Briggs Equation”<sup>3)</sup> | • Tier 1 Modelling PUF = 0 for all substances
  • Tier 2 Modelling with experimental derived PUF |

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2) Holdt et al. 2011: Recommendations for Simulations to Predict Environmental Concentrations of Active Substances of Plant Protection Products and their Metabolites in Groundwater (PECgw) in the National Assessment for Authorisation in Germany

<table>
<thead>
<tr>
<th>Current Status</th>
<th>Objectives</th>
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</table>
| • Lack of standardized, regulatory-accepted test systems for the experimental determination of PUF  
• Insufficient or conflicting data regarding the dependence of PUF on substance properties, crop type and pH of the soil solution | • Development and application of a regulatory accepted test system for the experimental determination of the PUF as a function of substance properties, crop type and pH of the soil solution |
Test Items:

<table>
<thead>
<tr>
<th></th>
<th>8 test items</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radio-label</td>
<td>$^{14}$C</td>
<td>7 labelled 1 non-labelled</td>
</tr>
<tr>
<td>Log Kow</td>
<td></td>
<td>0.16 - 3.9</td>
</tr>
<tr>
<td>pKa (4 dissociating test items)</td>
<td></td>
<td>2.30 - 5.1</td>
</tr>
<tr>
<td>$K_{oc}$</td>
<td>[mL/g]</td>
<td>&lt; 10 - &gt; 1000</td>
</tr>
<tr>
<td>Concentration in artificial pore water solution</td>
<td>[µg/L]</td>
<td>55 - 78</td>
</tr>
</tbody>
</table>
Test System Concept Part I:

- Intact plants: Tomato, wheat, OSR
- Cultivation in greenhouse: 5-6 weeks in natural soil (BBCH 23-51)
- Test vessel: 1-L amber glass - wide neck - Erlenmeyer flasks
- Artificial soil solution: 0.01 M CaCl$_2$ / buffered to pH 5.5, 6.5, 7.5
- Careful and quantitative rinsing of soil from the roots
- Transfer of the plants into the test solution with a defined concentration of test item (3 rep. / pH / plant)
- Incubation for 8 days in the greenhouse
- Determination of water uptake (gravimetric / volumetric) at day 0, 2, 5 and 8
- Determining the test item concentration at day 0, 2, 5, and 8
Test System Concept Part II:

- Controls without test item (influence of the test item on water uptake, pH monitoring)
- Controls without plants (sorption to glass walls, direct evaporation, stability of the test items)
- Concentration measurements by LSC or LC MS / MS
- Stability of the test items between Day 0 and Day 8 (Radio-HPLC)
- Desorption of test item adsorbed on roots with ACN/H2O
- Mass balance calculation (= remaining soil solution + plant material + desorption solution)
Test Conditions:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range:</th>
</tr>
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<tbody>
<tr>
<td>Air temperature ($^{\circ}$C)</td>
<td>20-24</td>
</tr>
<tr>
<td>Relative air humidity(%)</td>
<td>30-50</td>
</tr>
<tr>
<td>Light intensity (Lux) [5:00 - 21:00]</td>
<td>13000-18000</td>
</tr>
</tbody>
</table>
PUF calculation$^{1)}$: 

$$PUF = \frac{\ln\left(\frac{m_{\text{solution \_ 8}}}{m_{\text{solution \_ 0}}}\right)}{\ln\left(\frac{V_{\text{solution \_ 8}}}{V_{\text{solution \_ 0}}}\right)}$$

$m_{\text{solution \_ 0}} = \text{Initial mass of test item in soil solution } t_0$

$m_{\text{solution \_ 8}} = \text{mass of test item in soil solution } t_8$

$V_{\text{solution \_ 0}} = \text{Initial volume of soil solution } t_0$

$V_{\text{solution \_ 8}} = \text{Volume of soil solution } t_8$

Results: Validation Criteria

- pH values were stable over the test period
- Volume of water uptake > 200 mL (20%)
- No effect of test items on water uptake
- Evaporation was negligible (<1%)
- No sorption of test items on glass walls of the test vessels
- Test items were stable (with one exception)
- With one exception (86%) mass balances between 90-101%
- The fraction of adsorbed substance onto roots was considered as not taken up by the plant
Results: Water uptake by Transpiration stream

- Independent on crop type and pH, > 20% of the initial water volume was taken up by plants with the natural transpiration stream through the intact root system.
Overall, the influence of the pH on the PUF was low. In some cases significant differences* were indicated (even with non-dissociating substances), but were limited to single substance-pH-crop combinations.
Despite a few significant differences*, the influence of crop type on the PUF was marginal and limited to single substance-pH-crop combinations.
Within the given range of lipophilicity the PUFs were independent on Log Kow.

The overall mean PUF over all crops, pH levels and test items was 1 (± 0.25 SD)
Conclusions:

- A simple and reproducible test system with intact plants was established to determine PUFs as input parameter for “higher tier modelling”
- The PUFs were always > 0.5 and largely independent on the lipophilicity of the test items, pH and crop type
- The experimentally derived PUFs did not indicate any overestimation of plant uptake by using a default of 0.5 in pesticide leaching models
Thank you for your attention and applause to the EcoChemistry Team.

Victor Gourlay - PUF Ph.D. student.