Use of time dependent sorption in combination with field degradation half-lives for higher tier leaching assessment

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Background

- Time dependent sorption (TDS) is a relevant process that is often observed in laboratory and field experiments.

- TDS sorption can be used as higher tier process to refine the exposure assessment of pesticides (FOCUS, 2009 => Tier 2a).

- Draft guidance on design and evaluation of laboratory studies as well as on the use of TDS in exposure assessment was developed on behalf of UK-CRD and will be evaluated by EFSA (Beulke, van Beinum, 2012).

- The use of field studies for deriving TDS parameters or to be combined with TDS in exposure assessment is not foreseen in the guidance.
Background

The model

Equilibrium sorption domain (Freundlich)

Liquid phase

Solid phase

First order degradation

DegT50_{equ}

TDS parameters

No degradation

\( f_{NE} \) = ratio of NEQ-sorption and equilibrium sorption (e.g. \( K_{f,om-neq}/K_{f,om-equ} \))

K_{f,om-equ} 1/n

K_{f,om-neq} 1/n

K_{des} = rate constant of slow TDS

Non-Equilibrium sorption (TDS) domain
**Effect of TDS on leaching**

Realistic example of compound with borderline leaching properties

<table>
<thead>
<tr>
<th>Approach in tiered scheme according to FOCUS 2009</th>
<th>Assessment</th>
<th>DegT50</th>
<th>TDS</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tier 0)</td>
<td>modelling PEC$_{gw}$</td>
<td>laboratory</td>
<td>no</td>
<td>&gt; 1.0 µg/L</td>
</tr>
<tr>
<td>Tier 1)</td>
<td>modelling PEC$_{gw}$</td>
<td>field</td>
<td>no</td>
<td>&gt; 0.1 µg/L</td>
</tr>
<tr>
<td>Tier 2a) - i</td>
<td>modelling PEC$_{gw}$</td>
<td>lab with TDS</td>
<td>yes</td>
<td>&gt; 0.1 µg/L</td>
</tr>
<tr>
<td>Tier 2a) - ii</td>
<td>modelling PEC$_{gw}$</td>
<td>field with TDS</td>
<td>yes</td>
<td>&lt; 0.1 µg/L</td>
</tr>
<tr>
<td>Tier 3c) field leaching study</td>
<td>measurements</td>
<td>field*</td>
<td>yes*</td>
<td>&lt; 0.1 µg/L</td>
</tr>
<tr>
<td>Tier 4) targeted monitoring</td>
<td>measurements</td>
<td>field*</td>
<td>yes*</td>
<td>&lt; 0.1 µg/L</td>
</tr>
</tbody>
</table>

* all relevant processes considered
Arguments for consideration of TDS combined with DegT50 from field in exposure modelling

There is evidence that both processes are relevant for the transport of substances under field conditions (e.g. Boesten et al., 1989; Streck and Richter, 1999)

Comparison of modelling with experimental results showed justification for using TDS with field DegT50 (see example on previous slide)

From a technical point of view it is easily possible to implement TDS combined with field DegT50 in the models

Experience shows: If use of TDS is at the cost of using field DegT50 TDS will not (rarely) be used in regulatory assessments
Proposals for use of field half-lives combined with TDS

Approach 1) TDS parameters directly derived from field studies

Approach 2) $\text{DegT50}_{\text{equ}}$ estimated from field degradation studies under consideration of TDS parameters derived from laboratory aged sorption studies with same (or similar soil)
Field half-lives combined with TDS

Approach 1) TDS from field studies

- additional aqueous extraction of soil samples from field
- inverse modelling of field study with numerical model (e.g. PEARL with PEST) under consideration of TDS (no time-step-normalisation)
- use of estimated TDS parameters and \( \text{DegT50}_{\text{equ}} \) for exposure modelling
- input of geomean of rate constants such as \( \text{DegT50}_{\text{equ}} \) and desorption rate \( (k_{\text{des}}) \)
- input of arithmetic mean of the other TDS parameters \( (f_{\text{NE}}, K_{f,oc-\text{equ}}) \)
- quality criteria (RSE < 40%) from TDS lab guidance (Beulke and van Beinum, 2012) can be used but might be relaxed
Field half-lives combined with TDS

Approach 1) TDS directly from field studies – **Modelling case study**
with very good synthetic data set
(heterogeneity in real field might typically be greater)

- Hamburg scenario
- Dummy substance with TDS
  - DT50\textsubscript{equ} = 15 days
  - K\textsubscript{om,eq} = 30 L kg\textsuperscript{-1}
  - desorption rate = 0.01 day\textsuperscript{-1}
  - f_{NE} = 1.0
  - 1/n = 0.9
- Autumn application of 1 kg/ha
- Sampling = simulated (synthetic) values
  - 5 cm increments at 12 time points (DAT 0,1,4,8, MAT1,2,3,4,5,6,7,8)
  - down to 40 cm (= 8 increments)
  - 192 data points per realisation
  - -20% to +20% equally distributed random error => 10 realisations
Field half-lives combined with TDS

Approach 1) TDS from field studies – Modelling case study - results

- Graph shows one realisation of the fitted synthetic data
- Synthetic data and fits of total mass and liquid concentration in 0-5 cm layer
Approach 1) TDS from field studies – Modelling case study - results

- Graphs show one realisation of the fitted synthetic data
- Synthetic data and fits of total mass and liquid concentration in two layers

**Total mass**

**Liquid phase concentration**
Field half-lives combined with TDS

Approach 1) TDS from field studies – Modelling case study – results

<table>
<thead>
<tr>
<th>Parameter</th>
<th>True values</th>
<th>Mean of realisations (n=10)</th>
<th>CV of mean of realisations (n=10)</th>
<th>Mean of RSE of realisations (n=10)</th>
<th>Max of RSE of realisations (n=10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DegT50_{equ}</td>
<td>15.0</td>
<td>14.8</td>
<td>7.5%</td>
<td>2.78%</td>
<td>4.32%</td>
</tr>
<tr>
<td>M_{ini}</td>
<td>1.00</td>
<td>0.99</td>
<td>3.3%</td>
<td>0.62%</td>
<td>0.95%</td>
</tr>
<tr>
<td>Kom_{equ}</td>
<td>30.0</td>
<td>29.7</td>
<td>6.1%</td>
<td>1.26%</td>
<td>2.02%</td>
</tr>
<tr>
<td>f_{NE}</td>
<td>1.00</td>
<td>1.04</td>
<td>8.0%</td>
<td>8.02%</td>
<td>16.4%</td>
</tr>
<tr>
<td>k_{des}</td>
<td>0.010</td>
<td>0.011</td>
<td>34.0%</td>
<td>13.8%</td>
<td>27.1%</td>
</tr>
</tbody>
</table>

=> for this modelling example all parameters are below the quality criteria of the TDS guidance for lab studies
Interim conclusions for Approach 1

Deriving TDS parameters directly from field studies (Approach 1) is principally possible:

- The field study needs to be designed accordingly:
  - Additional water (CaCl\(_2\)) extraction
  - Good spatial resolution of depth concentration profile helpful
  - Quality criteria as for laboratory studies can be applied

Deriving TDS parameters directly from experimental field data will be difficult due to known heterogeneity with real data sets

=> there is a need for a alternative approach where TDS parameters from laboratory can be combined with ‘conventional’ field dissipation studies: Approach 2
Approach 2): Evaluating conventional field dissipation studies by using TDS parameters from laboratory studies

- TDS parameters determined in laboratory aged sorption studies according to design and quality criteria TDS guidance (Beulke, v. Beinum, 2012)

- Assumption that the TDS behaviour in laboratory is transferable to field conditions (=> same assumption as for equilibrium sorption)  
  => see also Hammel, 2010 (http://www.pfmodels.org/downloads/EMW5_14.pdf)

- Estimation of DegT50_{equ} from field study according to FOCUS_{kinetics} (2006). Consideration of EFSA guidance 2013 (DegT50 for modelling) possible.

- Inverse estimation of DegT50_{equ} by adjusting the TDS parameters in the model to the estimates from the laboratory TDS study
  - If possible (new studies) use same soil in aged sorption laboratory study as in field degradation study
  - for legacy studies the TDS parameters from the most similar soil of the laboratory aged sorption study should be used
Field half-lives combined with TDS

Approach 2) TDS from lab studies used for evaluation of field study

example with same soil in lab and field and very pronounced TDS

Results from aged sorption lab study (simultaneous fit of $M_{\text{tot}}$ and $C_{\text{liqu}}$)
Field half-lives combined with TDS

Approach 2) TDS from lab studies used for evaluation of field study

- *example with same soil in lab and field and very pronounced TDS*

Results from aged sorption laboratory study \( (f_{\text{NE}} \gg 1) \)

\[
\begin{align*}
\text{no TDS considered} & \quad \text{no TDS considered} \\
\text{TDS considered} & \quad \text{TDS considered}
\end{align*}
\]

- \( \text{no TDS considered} \)
  - \( \text{Apparent Kd calc} \)
  - \( \text{Apparent Kd obs} \)

- \( \text{TDS considered} \)
  - \( \text{Apparent Kd calc} \)
  - \( \text{Apparent Kd obs} \)

\[ \Rightarrow \text{TDS necessary to explain the observations of laboratory aged sorption study} \]

\[ \Rightarrow \text{TDS parameters were reliably estimated (RSE \leq 12\%)} \]
Field half-lives combined with TDS

Approach 2) TDS from lab studies used for evaluation of field study

(example with *same soil in lab and field* and *very pronounced TDS*)

**Results from field degradation study** (very pronounced TDS: \( f_{\text{NE}} \gg 1 \))

=> TDS necessary to explain the total mass of field study

=> \( \text{DegT50}_{\text{equ}} \) could be significantly estimated

\((\chi^2 \text{ error level} < 13\%, \ p\text{-value} < 0.001)\)
Interim conclusions for Approach 2

- Using TDS parameters from lab studies in the evaluation of conventional field dissipation studies (Approach 2) is principally possible
- If possible the same soil should be used
- The more pronounced the TDS is the more it will be reflected by the bi-phasic shape of the decline curve
- For less pronounced TDS the decline curve will only weakly affected
- Additional check of relevance of TDS using vertical transport in the field (depth residue profiles) possible
Field half-lives combined with TDS

Additional check of relevance (validation)

- Comparison of measured and simulated depth profiles with and without TDS
- Consideration of aged sorption should significantly improve the description of the measurements
- Only possible if downward transport of substance under the assumption of no TDS is simulated
- Only possible if the spatial resolution of sampling is sufficient (e.g., 5 to 10 cm samples)
Field half-lives combined with TDS}

Check of relevance (validation)
=> example from model case study with very good synthetic data set

Mass depth distribution profiles 77 days after treatment

no TDS considered in simulation

TDS considered in simulation
Field half-lives combined with TDS

Check of relevance (validation) => example from model case study with very good synthetic data set

Mass depth distribution profiles 161 days after treatment

no TDS considered in simulation

TDS considered in simulation
Field half-lives combined with TDS

Check of relevance (validation) – example from literature
Boesten JJTI, Van der Pas LTJ. and Smelt JH (1989).
Overall Conclusions

There is a strong need to combine TDS and degradation parameters from field studies in order to make use of TDS as higher tier option.

Deriving TDS parameters directly from field studies (Approach 1) is principally possible (but will be difficult with real data sets):
- The field study needs to be designed accordingly (extraction, spatial resolution)
- Quality criteria as for laboratory studies can be applied

Combining TDS parameters from laboratory with ‘conventional’ field dissipation studies (Approach 2) is possible:
- If possible the same/similar soils should be used in the lab and the field

Additional check of relevance of TDS in the field should be carried out:
- Considering TDS in the simulation of the field study should significantly improve the description of the measurements (decline curve or depth profile)
Thank you for your attention