Water-sed. studies for step 3 FOCUS

**SWS:**
Guidance of FOCUS Degradation Kinetics

Paulien Adriaanse en Wim Beltman
Alterra,
Wageningen University and Research Centre,
The Netherlands.
Introduction

- FOCUS Surface Water Scenarios since May 2003
- Tiered approach to assess aquatic exposure

- Input needed: pesticide properties and application pattern
- One of most difficult: degradation in water and in sediment

- Present approach Deg Kinetics + conclusions
  new development with TOXSWA + conclusions
Introduction

• When are degradation rates in water and in sediment important input?

(NOT for simple peaks after spray drift or ro/dr)

1. Chronic exposure
2. Peak caused by accumulation of concentrations in case of multiple applications on waterbodies with high residence times
3. Up-scaling above the edge-of-field level (transport times)
Introduction

• Basis for degradation rates: water-sediment study: test tubes in lab, controlled conditions, radio-labelled compound for: - degradation pathways and - persistence in surface water (mass measured in water and in sediment)
Introduction

- **Material Collection**
  - Sieving, mixing
- **Acclimation in Laboratory**
  - $20^\circ$ C dark
- **Water-Sediment System**
  - Water
  - Sediment
  - $^{14}$C pesticide
  - Volatiles trap
  - CO$_2$ trap
Introduction

- Necessary background:

  volatilisation

  sorption DOC, ss
  sorption sed

- So, dissipation DT50 ≠ DegT50!
Introduction

- Degradation rates: hard to estimate well

- FOCUS Deg Kinetics: guidance draft report 16 Jan for comment of MS this spring

- Guidance for use in step 3 FOCUS sws (level P-II), not for triggers, parent only
Guidance FOCUS Degradation Kinetics

• Level P-II: 2 procedures are needed

  1. Fit data water-sed study with SFO model

  2. Check obtained rates with TOXSWA runs for water-sed study
Guidance FOCUS Degradation Kinetics

**Kinetic Concept**

![Diagram of kinetic concept with compartments and equations]

**Generic Equations**

\[
\frac{dM_{wc}}{dt} = -r_{wc} M_{wc} + r_{sed} M_{sed} - k_{wc} M_{wc}
\]

\[
\frac{dM_{sed}}{dt} = -r_{sed} M_{sed} + r_{wc} M_{wc} - k_{sed} M_{sed}
\]

**Disappearance Graph**

![Graph showing data for wc and scd]

**Disappearance Times**

DegT50/90wc – calculate directly from the fit
DegT50/90sed – calculate directly from the fit
Guidance FOCUS Degradation

Kinetics

- Fit SFO
- Fit water and sediment simultaneously
- Fit 4 (or 3) parameters: $k_{wc}$, $k_{sed}$, $r_{wc}$ ($r_{sed}$)
- Fit until good fit: visual and statistical if necessary with constraints set by experts
Guidance FOCUS Degradation

Kinetics

• Particular attention if estimated values zero
  Behaviour in other studies (adsorption, hydrolysis, aerobic or unaerobic soil studies)
  Likely unrealistic -> redo fitting

• Three examples : 1 or 2 parameters (k) are 0
  Not likely-> expert sets constraints and redoes fitting
Guidance FOCUS Degradation Kinetics

- 4th example: Compound absorbing weakly to sediment

- **DegT50 in wc:** $\infty$
- **in sed:** 1.8

- **Step 1a:**
  - DegT50 in wc: $\infty$
  - in sed: 1.8

- **Step 1b:**
  - DegT50 in wc: 26.1 d
  - in sed: 4.3 d
Guidance FOCUS Degradation Kinetics

• Step 1a not acceptable (based on former work), so, take step 1b
• So, proposed fitting method alone seems not robust
• Possible reason: 4 parameters to be fitted at the same time, several solutions possible?
Guidance FOCUS Degradation

Kinetics

• Check if level P-II degradation rates in TOXSWA describe reasonably water-sed experiment

Level P-II: transfer water-sed 1st order
TOXSWA: transfer diffusion (Fick) + sorption to sed.

• If no good match with TOXSWA:
  3 steps procedure to redo fitting with TOXSWA coupled to PEST
Examples

- Compound 4, $K_{oc,soil} = 224$ L/kg
Examples

- Errors, compound 4, $K_{oc, soil} = 224$ L/kg
Examples

• Compound 3, $K_{oc,soil} = 76,000$ L/kg
Examples

- Errors, compound 3, $K_{oc,soil} = 76\ 000\ \text{L/kg}$
## DegT50 for water column and for sediment

<table>
<thead>
<tr>
<th>System</th>
<th>Level P-II</th>
<th>Optimisations TOXSWA-PEST</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Deg rates</td>
</tr>
<tr>
<td>Compound 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Koc</td>
<td>76 000 L/kg (soil)</td>
<td>-</td>
</tr>
<tr>
<td>Water</td>
<td>3.79 d</td>
<td>0.84 d</td>
</tr>
<tr>
<td>Sediment</td>
<td>50.6 d</td>
<td>590 d</td>
</tr>
<tr>
<td>Compound 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Koc</td>
<td>224 L/kg (soil)</td>
<td>-</td>
</tr>
<tr>
<td>Water</td>
<td>0.29 d</td>
<td>0.36 d</td>
</tr>
<tr>
<td>Sediment</td>
<td>0.30 d</td>
<td>0.03 d</td>
</tr>
</tbody>
</table>
Conclusions (1)

- 2 methods give different results, esp. for degradation rate in sediment
- no clear guidance on what to select for FOCUS sws
- entire procedure is laborious (2 models) and needs expert judgement
- is fitting with TOXSWA only an acceptable option?
Demonstration fitting with TOXSWA

- New development, TOXSWA coupled to PEST

- Use only TOXSWA instead of SFO model + TOXSWA

- Fit in 2 steps:
  1. $K_{oc,sed} = K_{oc,soil}$, optimise DegT50 for water and sediment
  2. Optimise $K_{oc,sed}$, both DegT50s simultaneously with range set for $K_{oc,sed}$ (e.g. $\frac{1}{2}$-2 $K_{oc,soil}$)
Fitting with TOXSWA

- Advantages of using TOXSWA:
  - physical basis
  - standardized, no expert judgement needed
  - 3 instead of 4 parameters to fit, (of which 1 uses info from soil studies)
  - also used in FOCUS sws
Fitting with TOXSWA

- Disadvantages of TOXSWA:
  - User-friendliness of fitting procedure?
  - No solution for DegT50s of metabolite
Fitting with TOXSWA

• Parameterise TOXSWA for water-sediment system:
  - system dimensions, sed properties
  - pesticide properties

• Parameterise PEST (2x):
  - select parameters
  - give water and sediment data equal weights

• Run TOXSWA, coupled to PEST (2x)
• Examine graphical output
Fitting with TOXSWA

- At present: TOXSWA 1.2 coupled to PEST used (Annex 11 of FOCUS Deg Kin report)

- From summer 2004 in: FOCUS_TOXSWA_2.2.2
  
  ( = FOCUS-TOXSWA_1.1.1 plus
  - current bugs repaired and
  - simulation of water-sediment studies made easier
  (coupled to PEST))
Create project (copy example water-sed)

<table>
<thead>
<tr>
<th>Name</th>
<th>Description</th>
<th>Last modified</th>
<th>SWASH project?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bernd_metab</td>
<td>metabolites SWASH incorrect</td>
<td>20-11-2003 17:49:28</td>
<td>True</td>
</tr>
<tr>
<td>project1</td>
<td>van testplan</td>
<td>25-11-2003 17:07:01</td>
<td>True</td>
</tr>
<tr>
<td>project2</td>
<td>proj2vantageplanv3</td>
<td>04-12-2003 16:45:22</td>
<td>True</td>
</tr>
<tr>
<td>project_sub_3</td>
<td>project3vantageplan</td>
<td>04-12-2003 16:51:32</td>
<td>True</td>
</tr>
<tr>
<td>c_project1</td>
<td>copy_van testplan</td>
<td>02-12-2003 15:31:16</td>
<td>False</td>
</tr>
<tr>
<td>c_project2</td>
<td>copy_project3vantageplan</td>
<td>04-12-2003 12:26:55</td>
<td>False</td>
</tr>
<tr>
<td>c_project3</td>
<td>copy_project3vantageplan</td>
<td>05-12-2003 09:52:43</td>
<td>False</td>
</tr>
<tr>
<td>testdatabase</td>
<td>testdatabase1</td>
<td>30-01-2004 12:18:49</td>
<td>True</td>
</tr>
<tr>
<td>Catania_1</td>
<td>Example project, water-sediment</td>
<td>30-01-2004 12:20:22</td>
<td>False</td>
</tr>
<tr>
<td>Catania_2</td>
<td>Example project, water-sediment</td>
<td>13-02-2004 13:23:34</td>
<td>False</td>
</tr>
</tbody>
</table>
Two runs to optimise
Parameterise system (ca 10 values)
Parameterise substance (ca 8 values)
Close TOXSWA application
Run PEST coupled to TOXSWA

- Parameterise TOXSWA_to_PEST application:
  - enter all measured data (equal weight)

- 1. enter $K_{oc,soil}$, 2 initial DegT50s+range
- 2. enter $K_{oc,soil}$ +range, 2 initial DegT50s+range

- Start optimising 2 or 3 parameters
- Extract results (DegT50s, $K_{oc,sed}$ plus uncertainty: errors, confidence intervals,..)
Conclusions (2)

• TOXSWA is straightforward (no reliance on expert judgement)
  - straightforward ≠ correct !,
    assumptions in model concept, $K_{oc,\text{soil}} \approx K_{oc,\text{sed}}$
    b.d., porosity, ..

• Visual comparison remains important (degradation lines + fit errors)

• Both methods laborious + not simple -> decision tree on need for water-sediment study analysis would help