

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 appln 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. Upscaling above the edge-of-field level (transport times)

Introduction

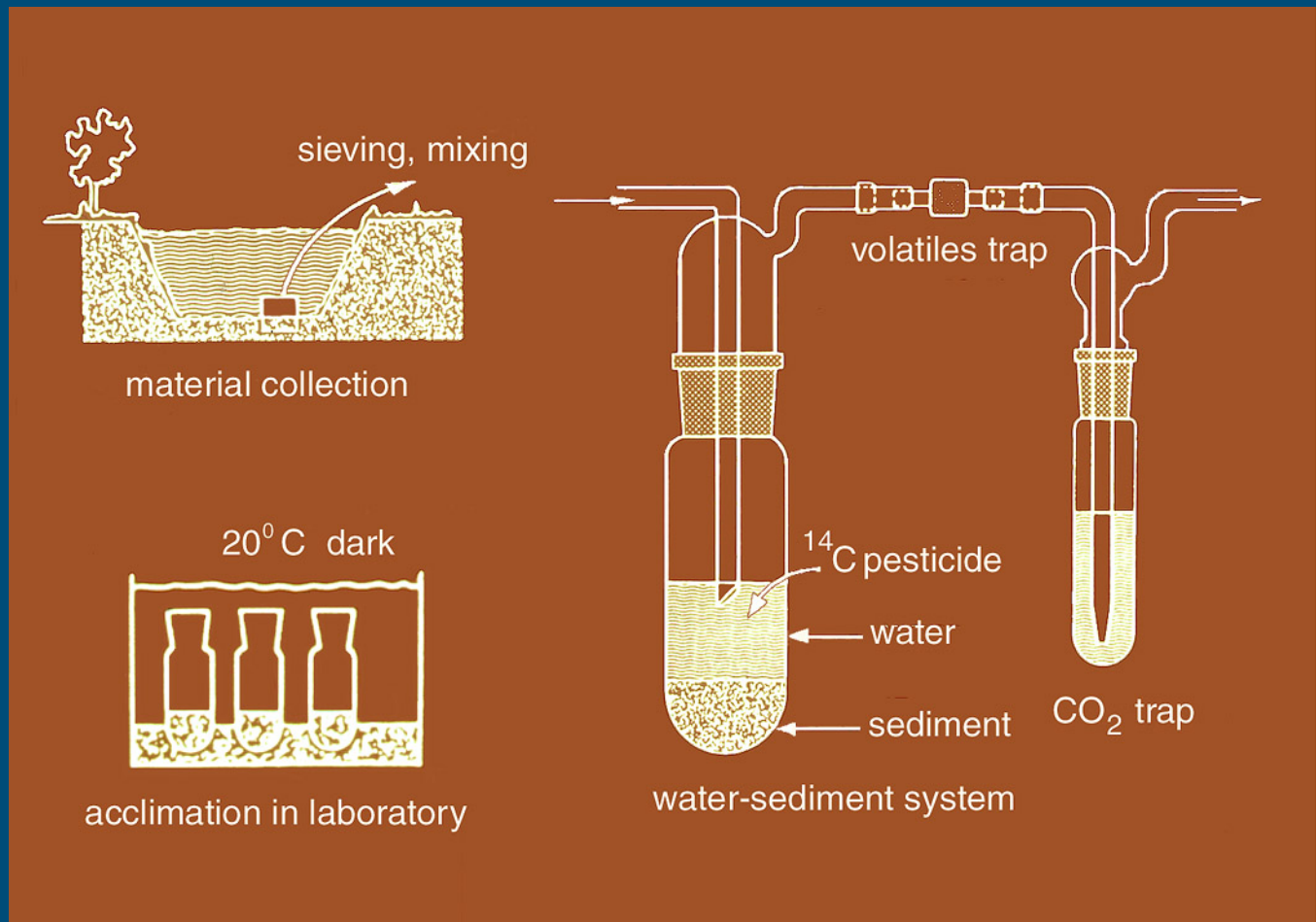
- Basis for degradation rates:
water-sediment study:
test tubes in lab,

controlled conditions,

radio-labelled compound for:
 - degradation pathways and
 - persistence in surface water
(mass measured in water and in sediment)

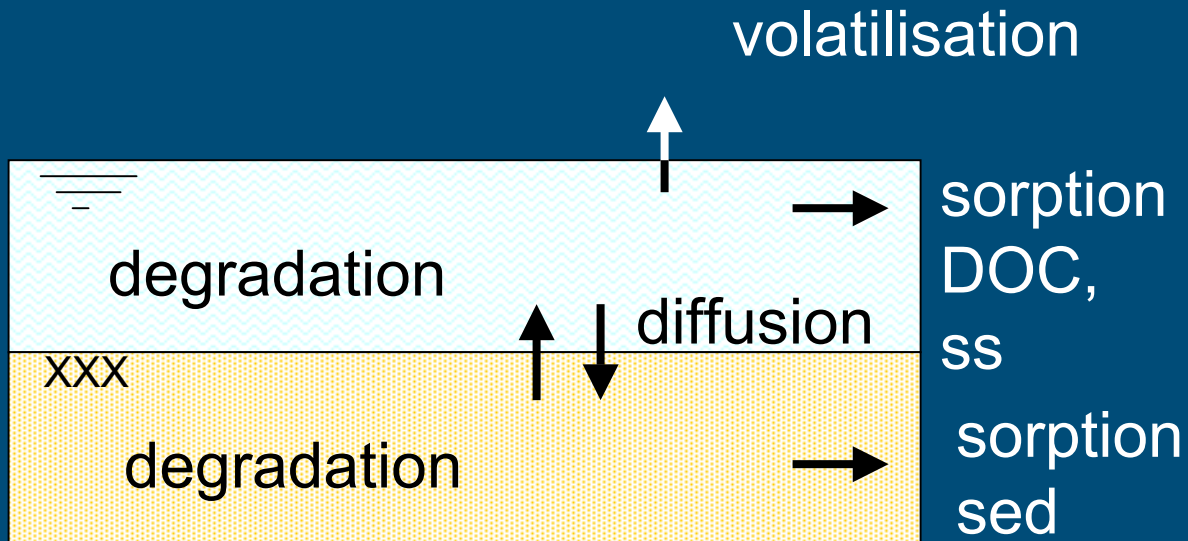


Introduction



Introduction

- Necessary background:



- So, dissipation $DT50 \neq DegT50$!

Introduction

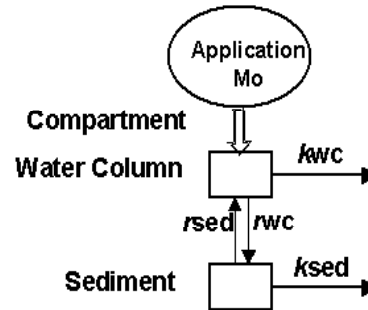
- Degradation rates: hard to estimate well
- FOCUS Deg Kinetics: guidance draft report 16 Jan for comment of MS this spring
- Guidance for use in step 3 FOCUS sws (level P-II), not for triggers, parent only

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

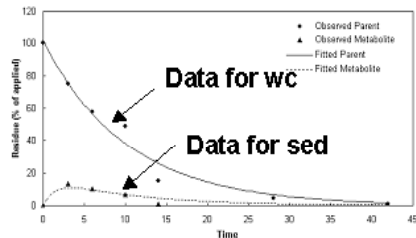


Generic Equations

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

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

Disappearance Graph



Disappearance Times

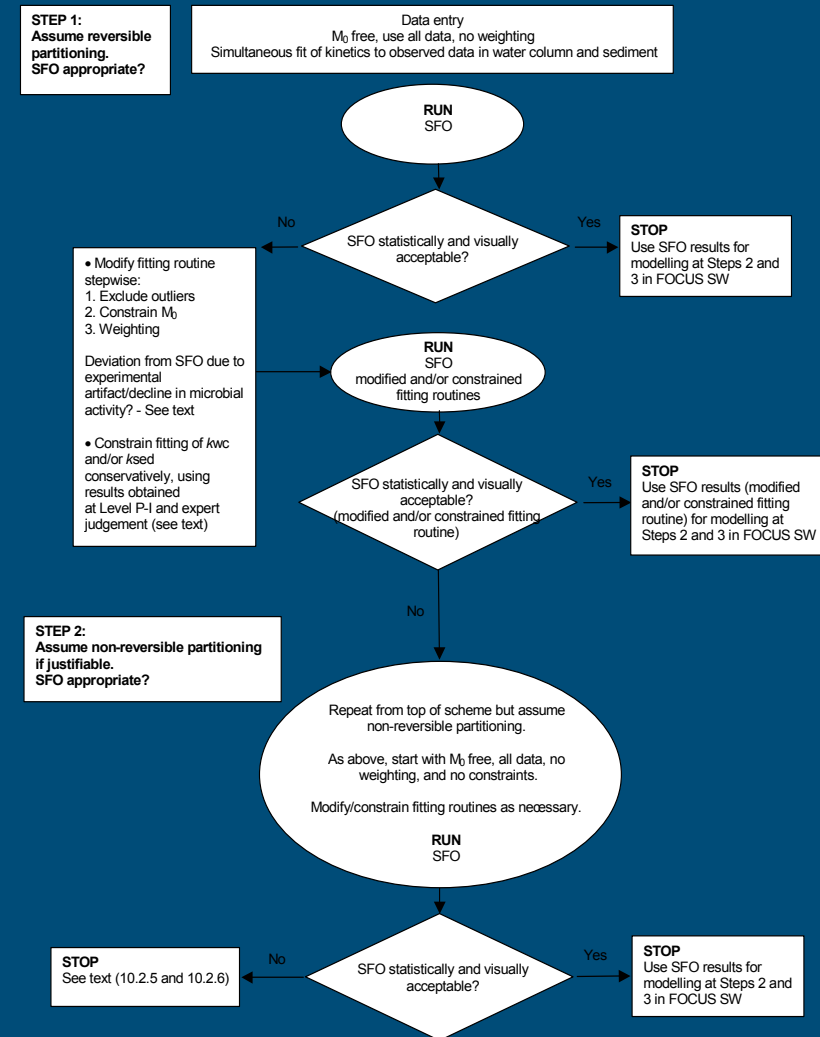
DegT50/90wc – calculate directly from the fit

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

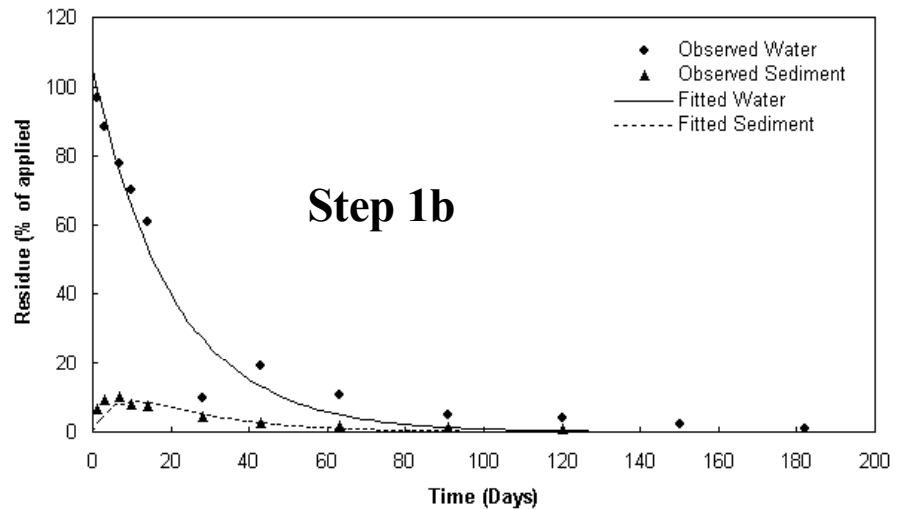
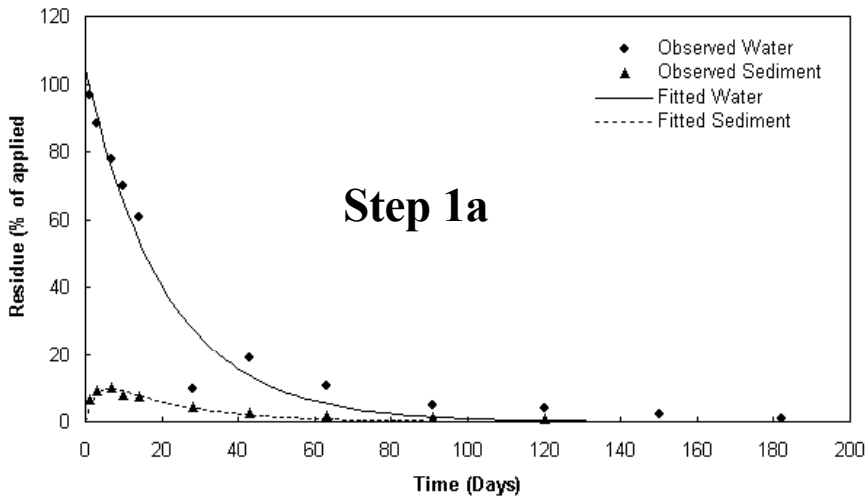


Guidance FOCUS Degradation Kinetics

- Particular attention if estimated values zero
Behaviour in other studies (adsorption, hydrolysis, aerobic or anaerobic 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: ∞
- in sed: 1.8

26.1 d

4.3 d

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- 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 degr.rates in TOXSWA describe reasonably water-sed experiment

Level P-II: transfer water-sed 1st order

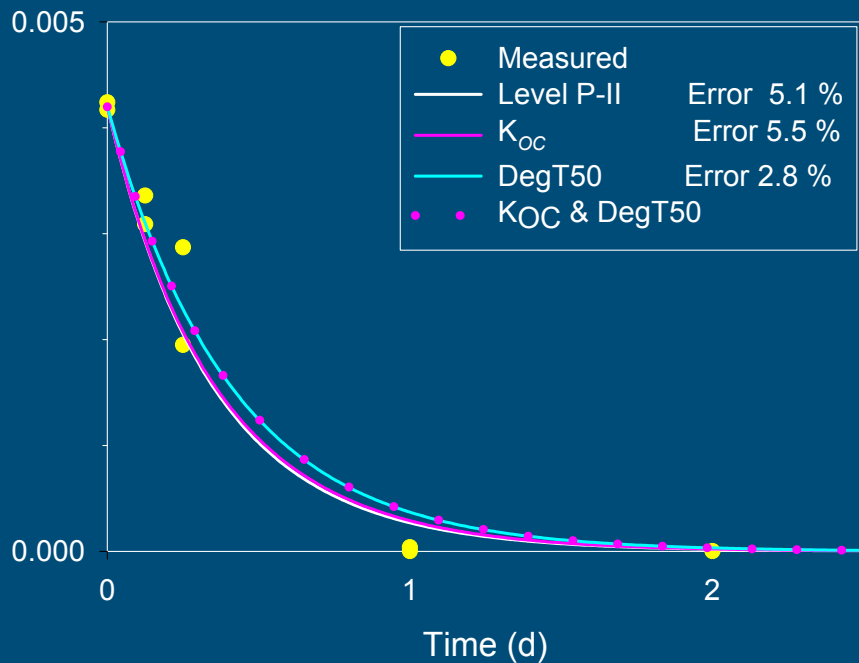
TOXSWA: transfer diffusion (Fick) + sorption to sed.

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

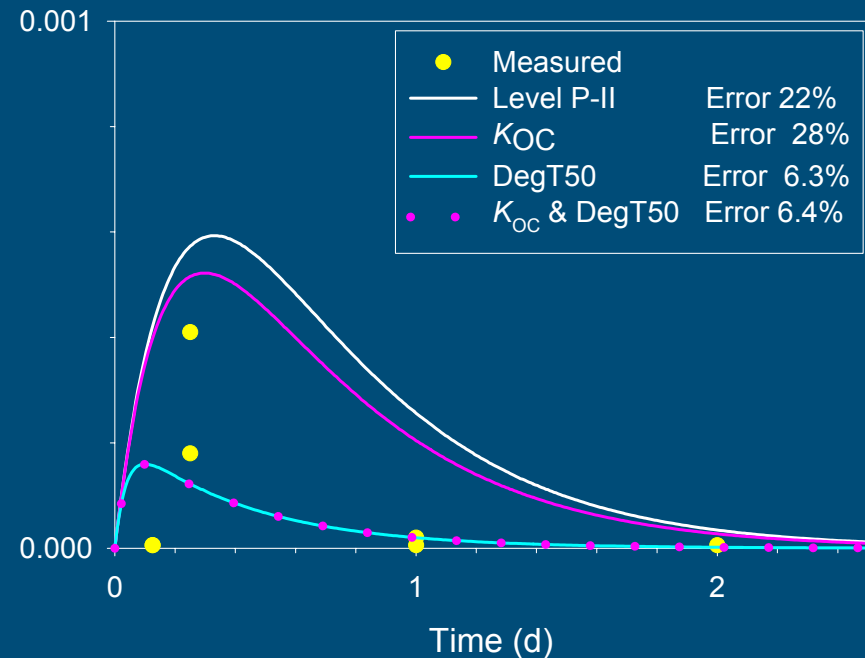
Examples

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

Concentration (mg/L)



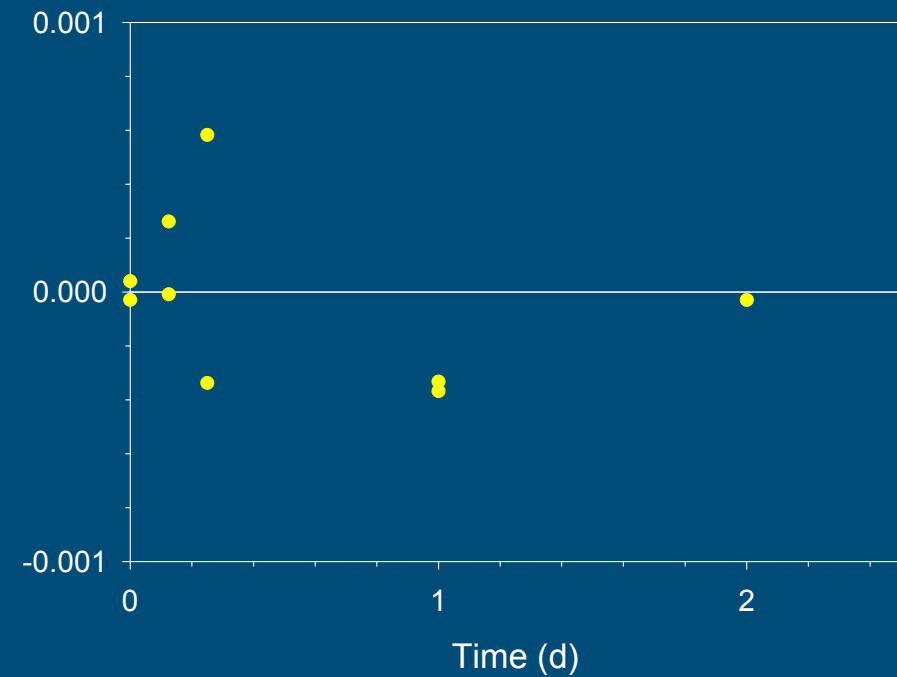
Concentration (mg/dm³)



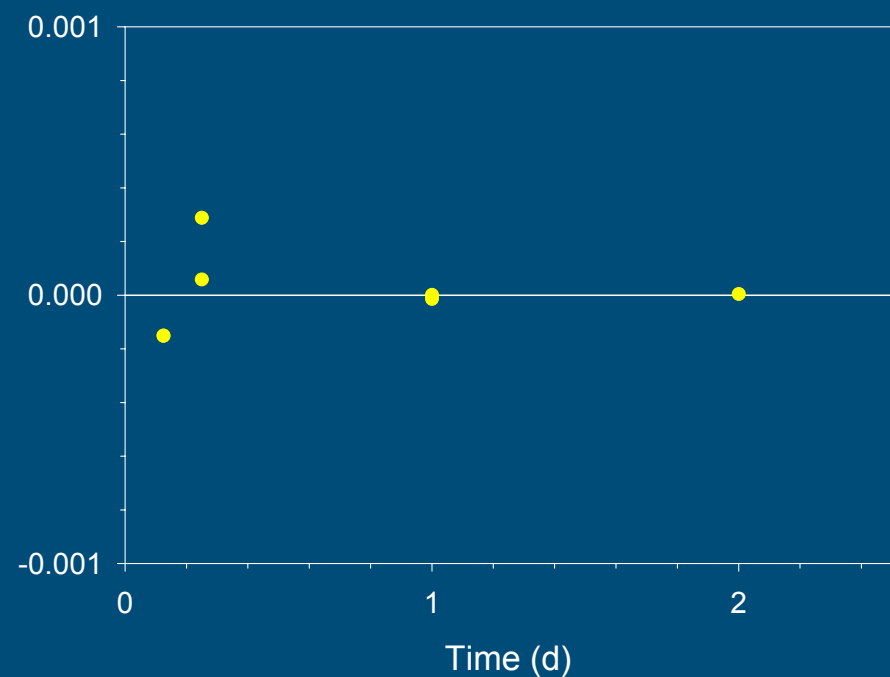
Examples

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

Difference (mg/L)



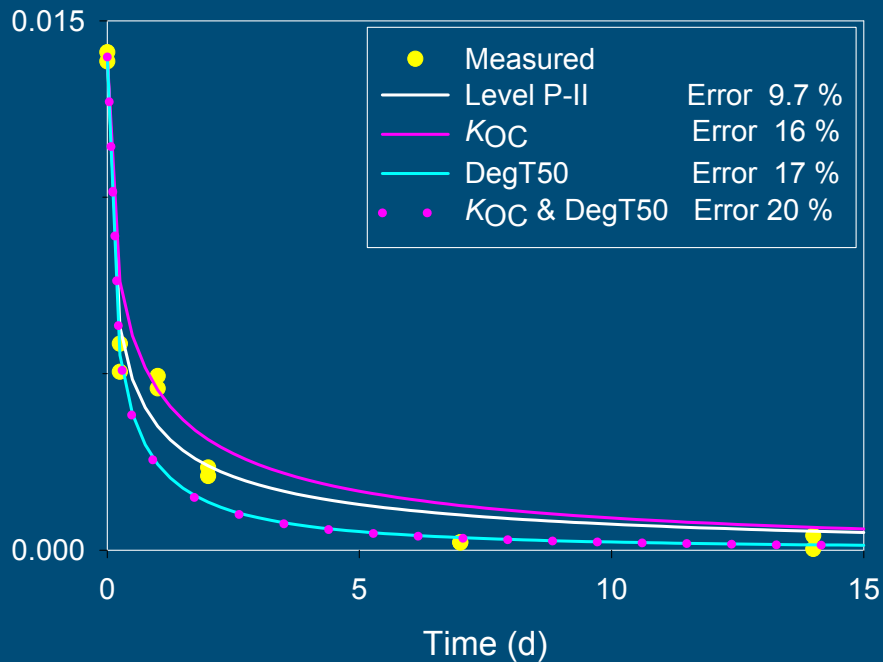
Difference (mg/dm³)



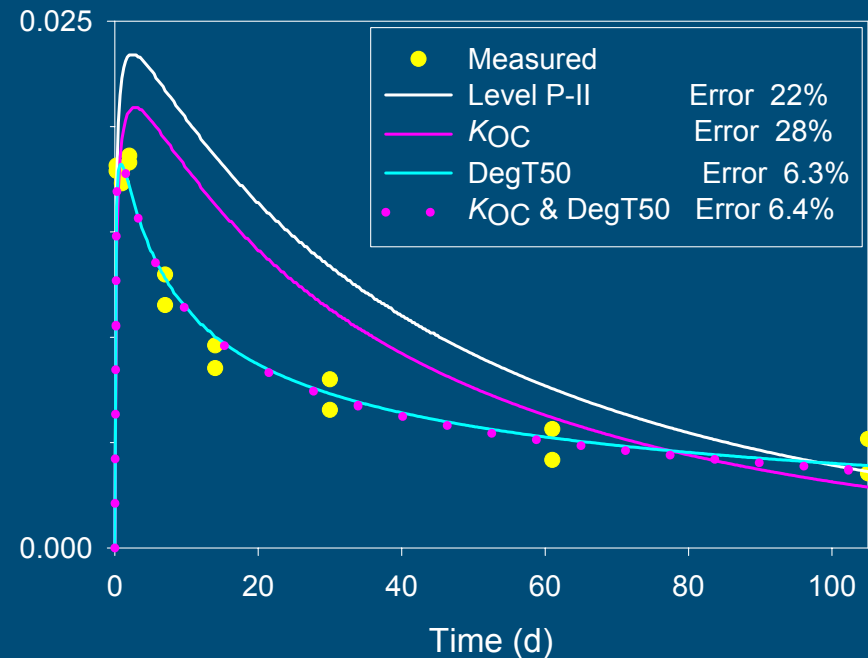
Examples

- Compound 3, $K_{oc,soil} = 76\ 000\ \text{L/kg}$

Concentration (mg/L)



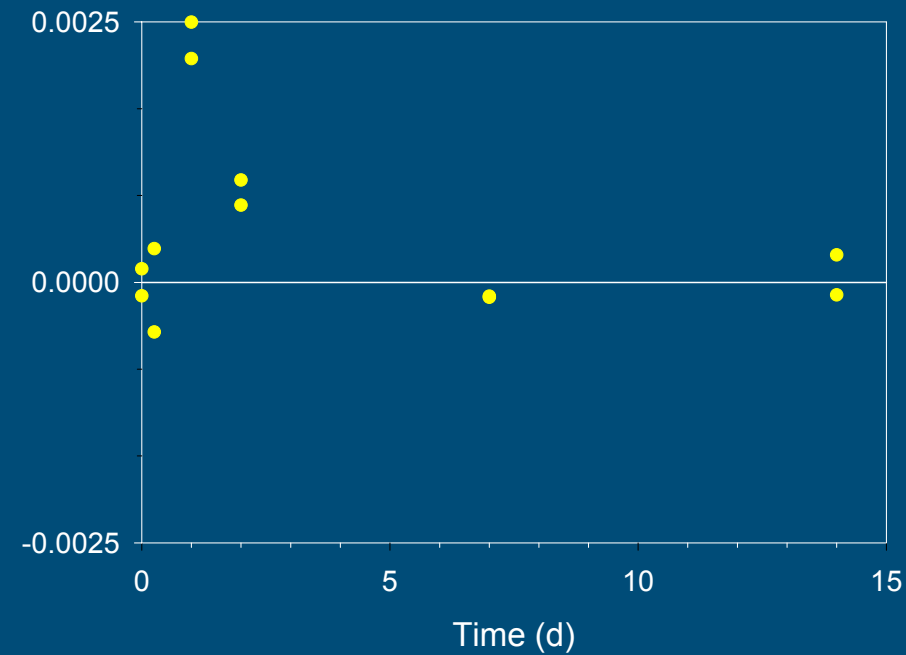
Concentration (mg/dm³)



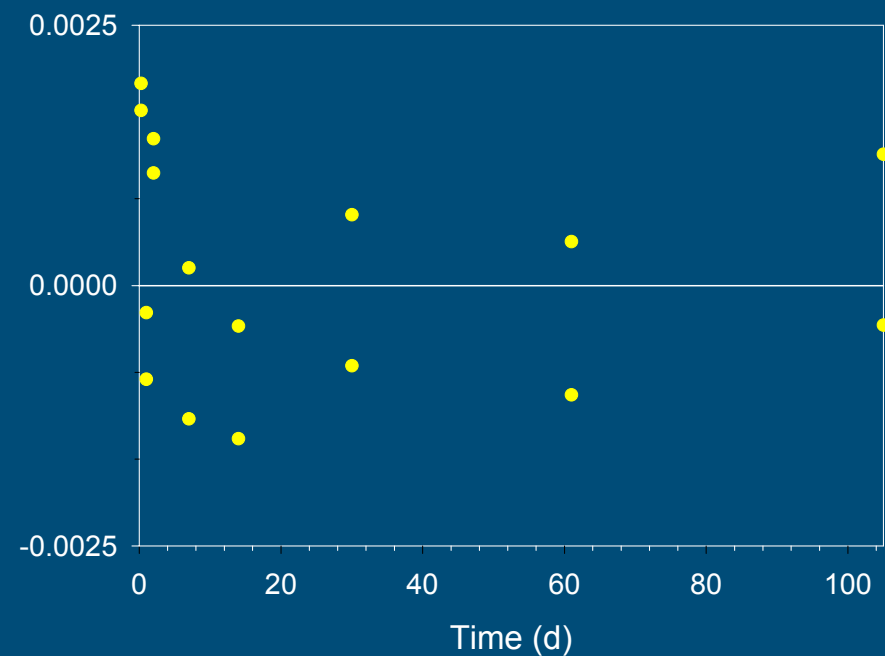
Examples

- Errors, compound 3, $K_{oc,soil} = 76\ 000\ \text{L/kg}$

Difference (mg/L)



Difference (mg/dm³)



Examples

- Results level P-II and TOXSWA-PEST

DegT50 for water column and for sediment

System	Level P-II	Optimisations TOXSWA-PEST	
		Deg.rates	Deg.rates & Koc
Compound 3			
Koc	76 000 L/kg (soil)	-	80 769 L/kg (sed)
Water	3.79 d	0.84 d	0.81 d
Sediment	50.6 d	590 d	395 d
Compound 4			
Koc	224 L/kg (soil)	-	143 L/kg (sed)
Water	0.29 d	0.36 d	0.35 d
Sediment	0.30 d	0.03 d	0.03 d

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)

TOXSWA - Projects

Select TOXSWA project

Name	Description	Last modified	SWASH project?
Bernd_metab	metabolites SWASH incorrect	20-11-2003 17:48:28	True
project1	van testplan	25-11-2003 17:07:01	True
project2	proj2vantestplanv3	04-12-2003 16:45:22	True
project_sub_3	project3van testplan	04-12-2003 16:51:32	True
c_project1	copy_van testplan	02-12-2003 15:31:16	False
c_project_sub_3	copy_project3van testplan	04-12-2003 12:26:55	False
c_project2	copy_proj2vantestplanv3	05-12-2003 09:52:43	False
testdatabase	testdatabase1	30-01-2004 12:18:49	True
Catania_1	Example project, water-sediment	30-01-2004 12:20:22	False
Catania_2	Example project, water-sediment	13-02-2004 13:23:34	False

Open selected project: OK Copy

Name:

Description:

Go to: SWASH PEARL IMAG Drift Calc.

Help Exit

Two runs to optimise

The screenshot displays the TOXSWA software interface for a project named 'Catania_2'. The 'Browse Runs' panel shows a table of runs, with 'RunKoc_opt' selected. The 'Edit Run' panel shows configuration options for the selected run, including scenario details and pesticide parameters.

TOXSWA project : Catania_2

File Edit Scenario View Runs Graphs Help

Projects View Inputfile Calculation Help Close

Browse Runs

RunID	Selected	Focus run	Name	Results
100000151	Yes	False	RunKoc_soil	Not available
100000152	Yes	False	RunKoc_opt	Not available

Report
Graphs
 All files for graphical output selected
Copy
◀ ▶ + - ✓ ✕

Edit Run

Scenario Simulation Control Output Control Run Status

Name: RunKoc_opt Comments...

Scenario

Location: Wat-sed compound 4 FOCUS Deg Kin ...
Water body: c water
Crop:

Pesticide and scenario dependent

Substance: compound 4 FOCUS Deg ...
Application scheme: Default_Scheme ...
Initial conditions for pesticide...

Parameterise system (ca 10 values)

Toxswa - Locations [X]

Browse Locations

Code	Water body code	Name	Country
R1	focus_pond	R1 (Meteo station: Weiherbach)	
R1	focus_stream	R1 (Meteo station: Weiherbach)	
R2	focus_stream	R2 (Meteo station: Porto)	
R3	focus_stream	R3 (Meteo station: Bologna)	
R4	focus_stream	R4 (Meteo station: Roujan)	
Vredepeel	Vredepeel_ditch	Vredepeel	The Netherlands
C4_system	c4_system	Wat-sed compound 4 FOCUS Deg Kin	EU
C4_system1	c4_system1	Wat-sed compound 4 FOCUS Deg Kin	EU

Comments [X] Copy [Left] [Right] [Plus] [Minus]

Edit Location

Name: Longitude (dec. degrees, East positive):

Code: Latitude (dec. degrees):

Country: Altitude (m):

Water body: ... Seepage / Concentration

Sediment: ... Seepage (mm/d):

Hydrology: Pond Watercourse Concentration (mg/L):

...

Meteo station: ...

[?] Help [Close]

Parameterise substance (ca 8 values)

Toxswa - Substance

Browse Substances

Code	Name
prosulfo	prosulfocarb
sub_1	sub_1 voor testplan
sub_2	sub_2 voor testplan
sub_3	sub_3 voor testplan
testP1	testwaterslib1
comp_4	compound 4 FOCUS Deg

Copy

Navigation: Previous, Next, Add, Subtract, Confirm, Cancel

Comments

Edit Substance

General | Sorption | Transformation

Code :

Name :

Molar mass (g/mol) :

Saturated vapour pressure (Pa) : measured at (°C) :

Molar enthalpy of vaporisation (J/mol) :

Solubility in water (mg/l) : measured at (°C) :

Molar enthalpy of dissolution (J/mol) :

Diffusion coefficient in water (m²/d) :

Help Close

Close TOXSWA application

The screenshot displays the TOXSWA application window titled "TOXSWA project : Catania_2". The interface includes a menu bar (File, Edit Scenario, View, Runs, Graphs, Help) and a toolbar with icons for Projects, View Inputfile, Calculation, Help, and Close. The main area is divided into two sections: "Browse Runs" and "Edit Run".

Browse Runs

RunID	Selected	Focus run	Name	Results
100000151	Yes	False	RunKoc_soil	Not available
100000152	Yes	False	RunKoc_opt	Not available

Buttons: Report, Graphs, All files for graphical output selected (checkbox), Copy, and navigation controls (back, forward, zoom in, zoom out, check, close).

Edit Run

Scenario | Simulation Control | Output Control | Run Status

Name: RunKoc_opt [Comments...]

Scenario

Location: Wat-sed compound 4 FOCUS Deg Kin [...]
Water body: c_water
Crop: []

Pesticide and scenario dependent

Substance: compound 4 FOCUS Deg [...]
Application scheme: Default_Scheme [...]
[Initial conditions for pesticide...]

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, $K_{oc,soil}$ plus uncertainty: errors, confidence intervals,..)

Conclusions (2)

- TOXSWA is straightforward (no reliance on expert judgement)
 - straightforward \neq correct !,
assumptions in model concept, $K_{oc,soil} \approx K_{oc,sed}$
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