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.

ALTERRA
GREEN WORLD RESEARCH

WAGENINGEN UR

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)

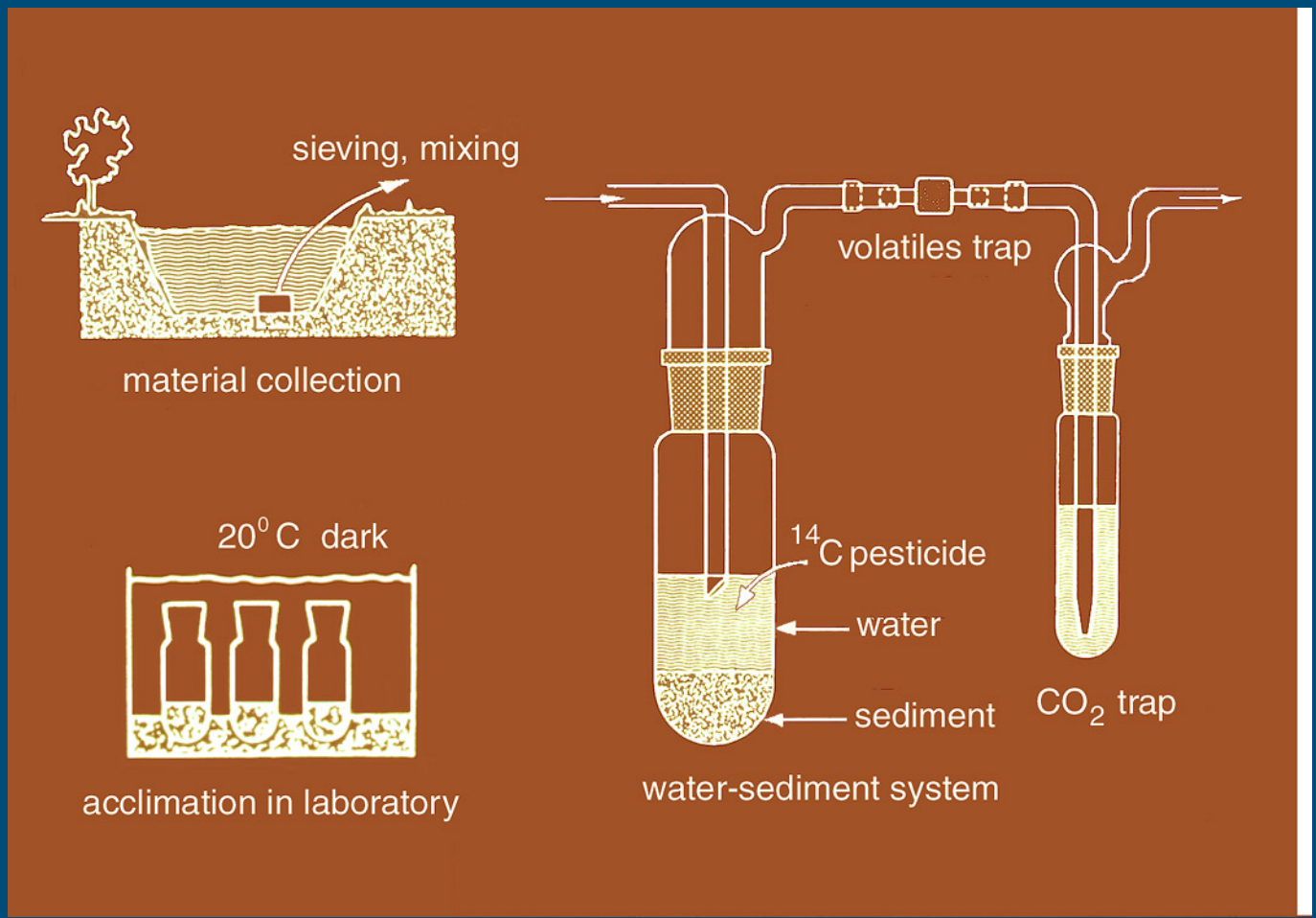
Introduction

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

  controlled conditions,

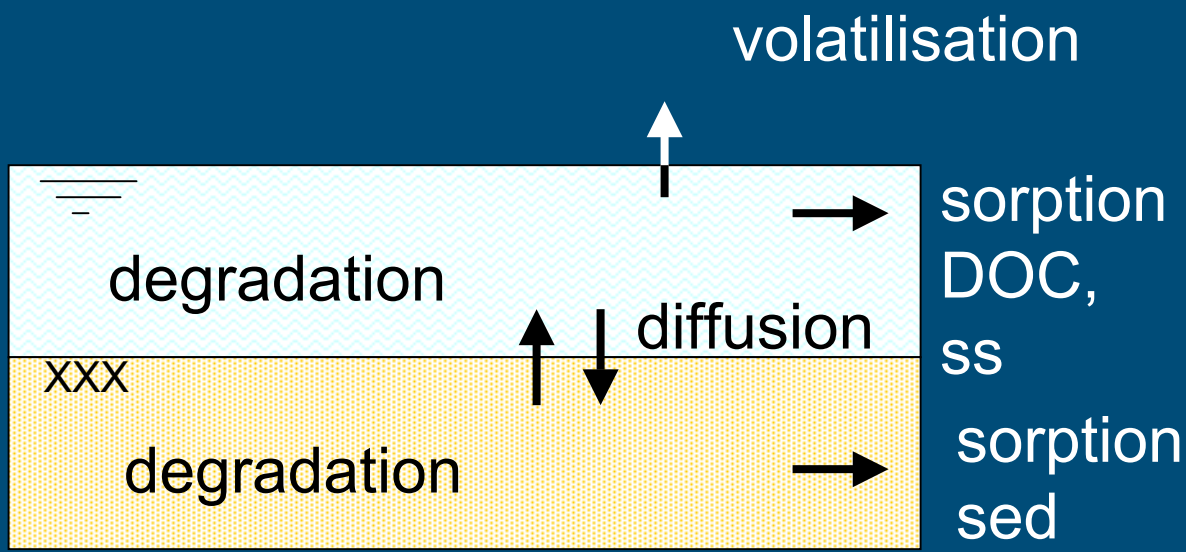
  radio-labelled compound for:
  - degradation pathways and
  - persistence in surface water
    (mass measured in water and in sediment)

Introduction



Introduction

- Necessary background:



- So, dissipation DT50 ≠ 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

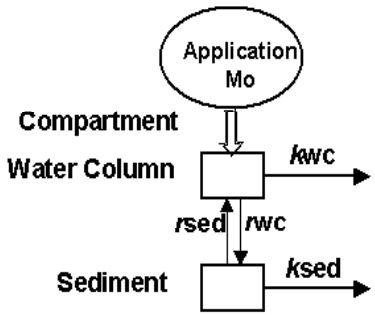
- Level P-II: 2 procedures are needed

  1. Fit data water-sed study with SFO model

  2. Check obtained rates with TOXSWA runs for water-sed study

Guidance FOCUS Degradation Kinetics

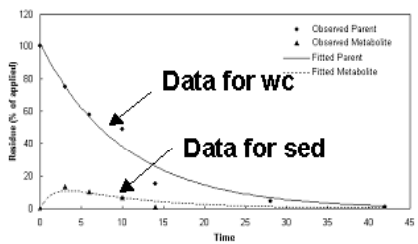
Kinetic Concept



Generic Equations

$$\frac{dMwc}{dt} = -rwc\ Mwc + rsed\ Msed - kwc\ Mwc \qquad \frac{dMsed}{dt} = -rsed\ Msed + rwc\ Mw - ksed\ Msed$$

Disappearance Graph



Disappearance Times

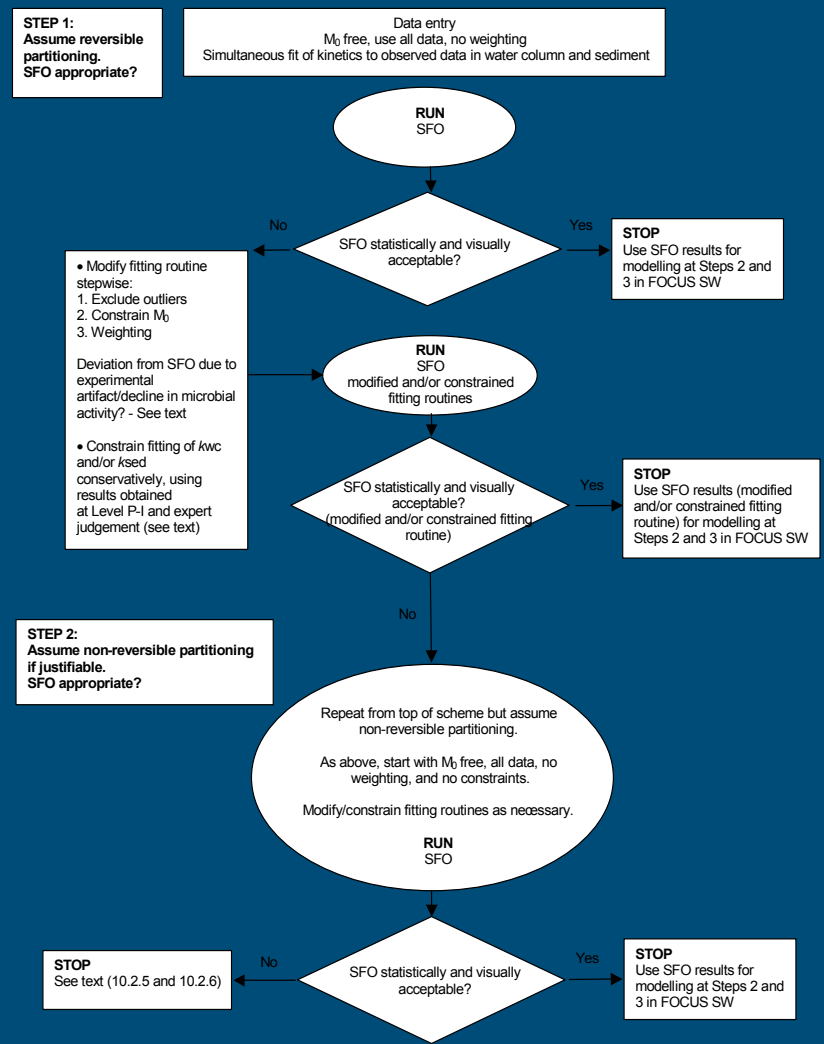
DegT50/90wc – calculate directly from the fit

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 untill good fit:
  visual and statistical
  if necessary with constraints
  set by experts



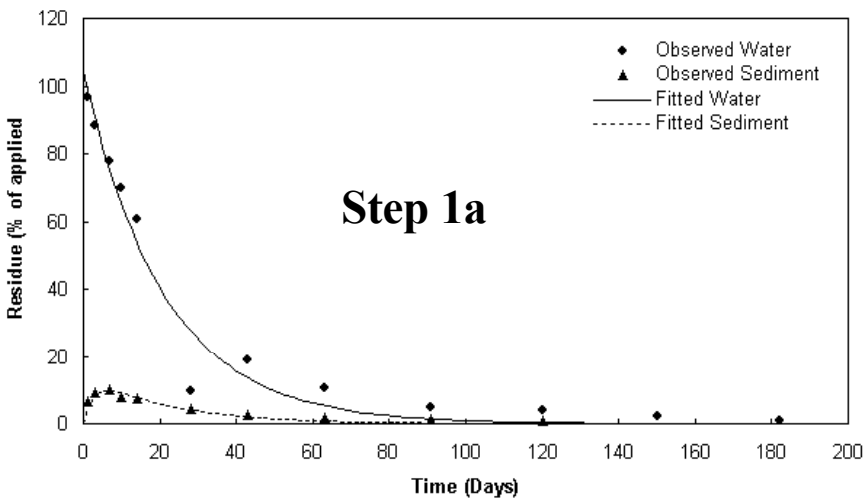
Guidance FOCUS Degradation Kinetics

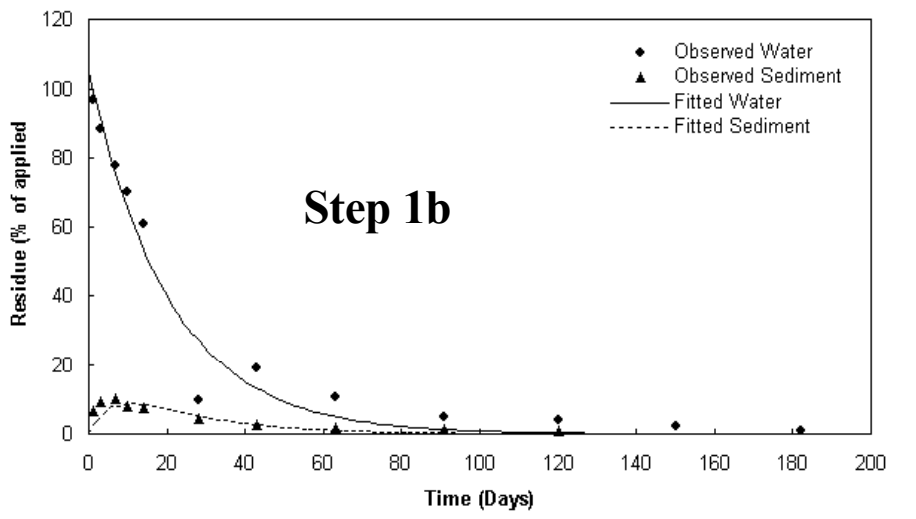
- Particular attention if estimated values zero
  Behaviour in other studies (adsorption, hydrolysis, aerobic or unaerobic soil studies)
  Likely unrealistic -> redo fitting

- 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: ∞ 26.1 d
- in sed: 1.8 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

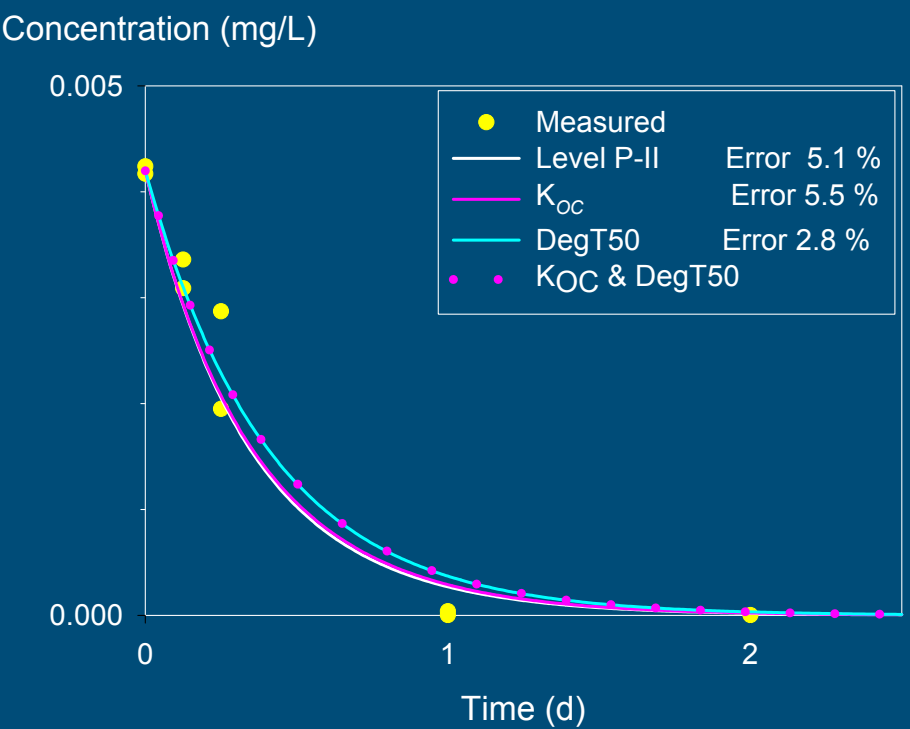
- Check if level P-II degr.rates in TOXSWA describe reasonably water-sed experiment

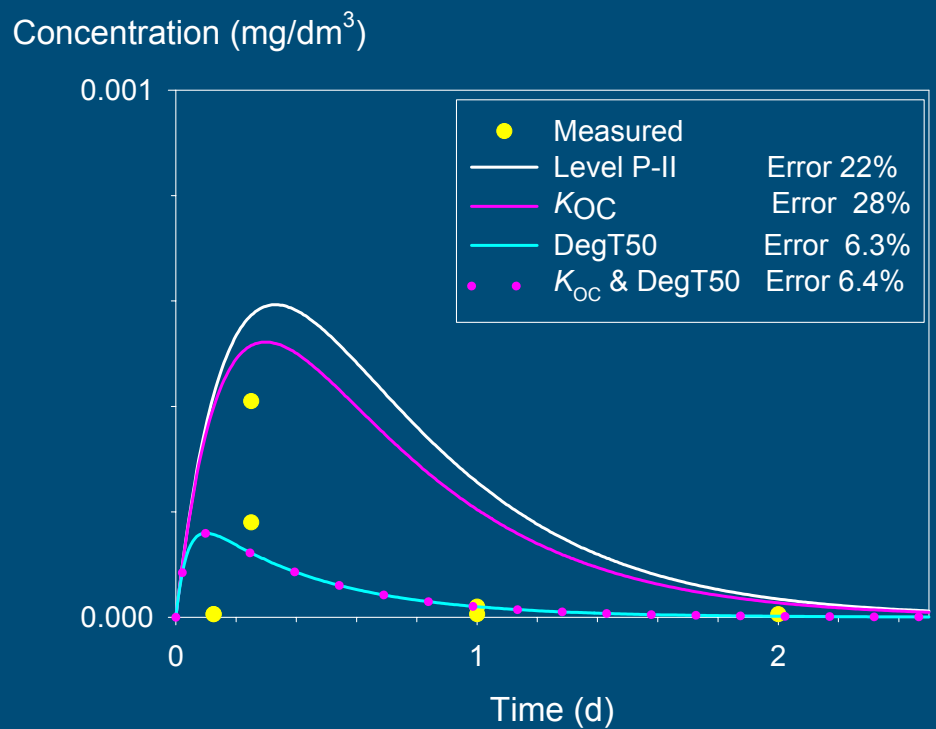
  Level P-II: transfer water-sed 1st order
  TOXSWA: transfer diffusion (Fick) + sorption to sed.

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

Examples

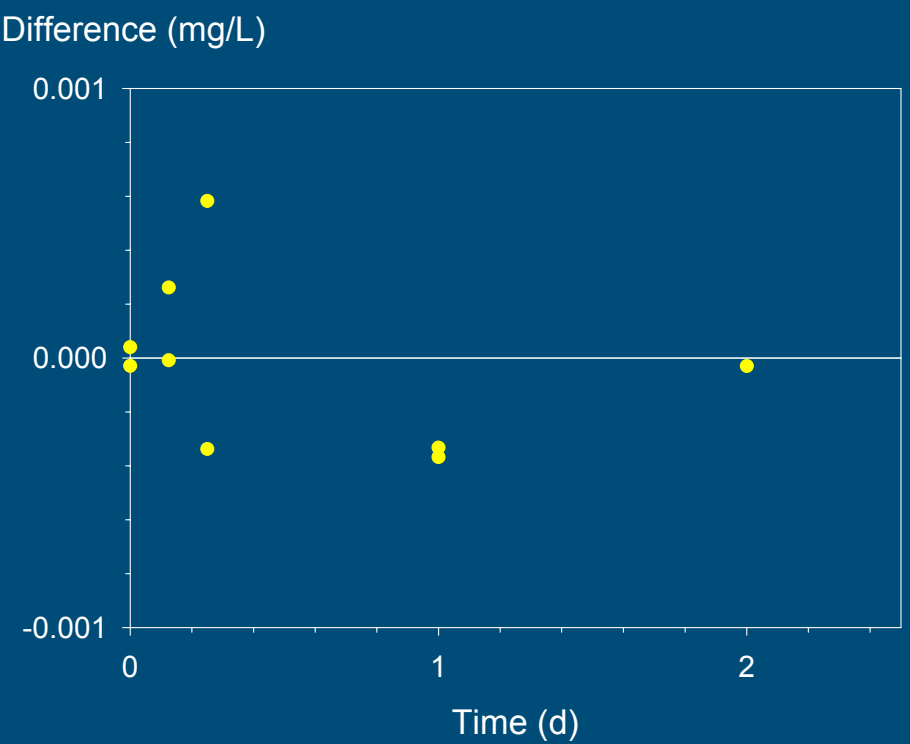
- Compound 4, $K_{oc,soil}$ = 224 L/kg

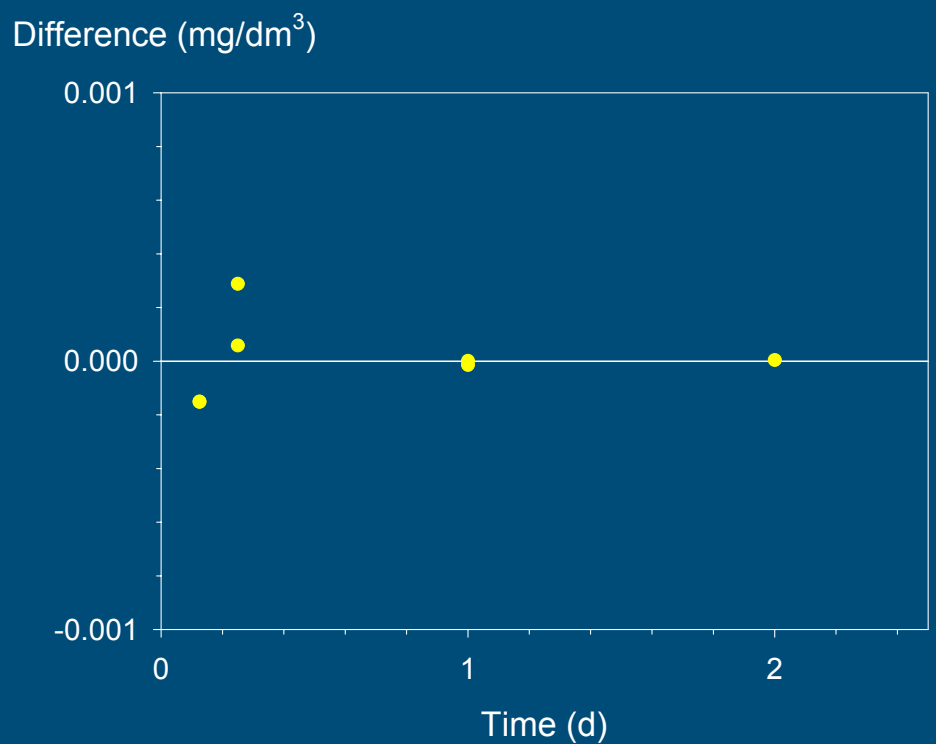




Examples

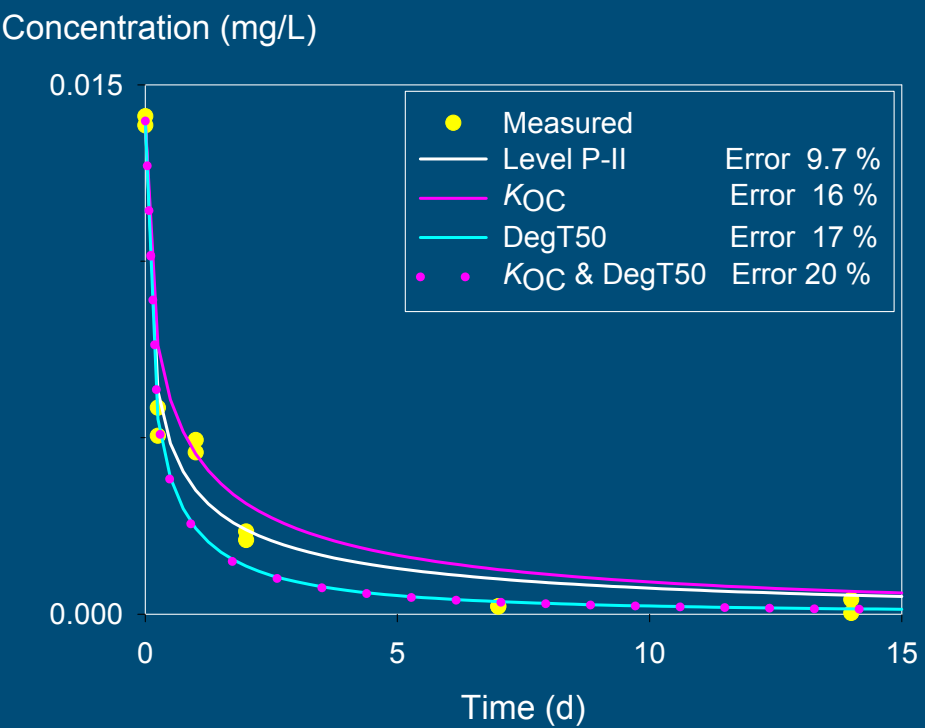
- Errors, compound 4, $K_{oc,soil}$ = 224 L/kg

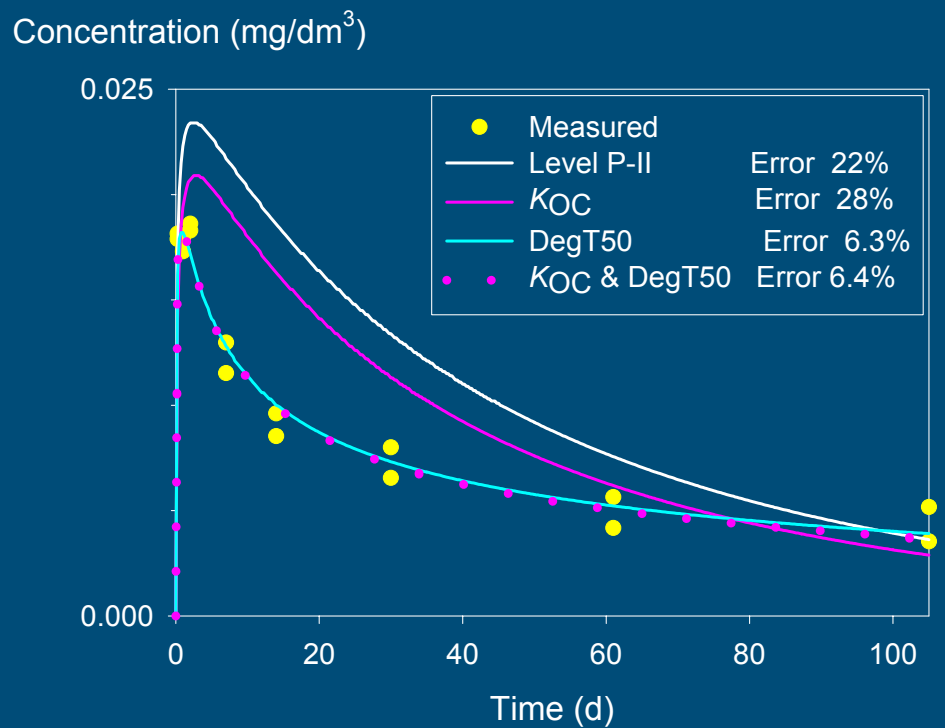




Examples

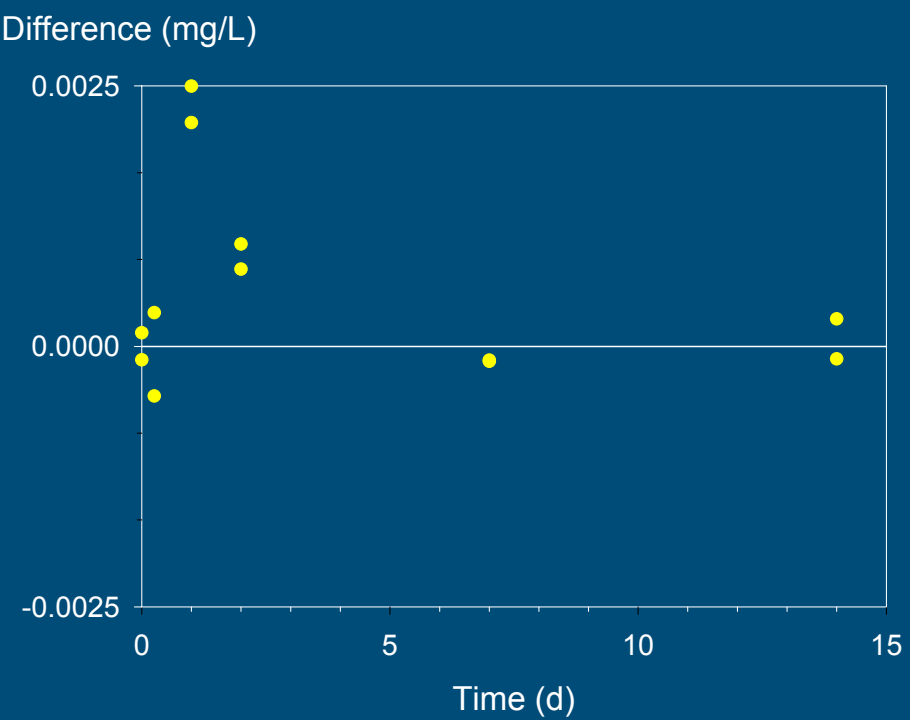
- Compound 3, $K_{oc,soil}$ = 76 000 L/kg

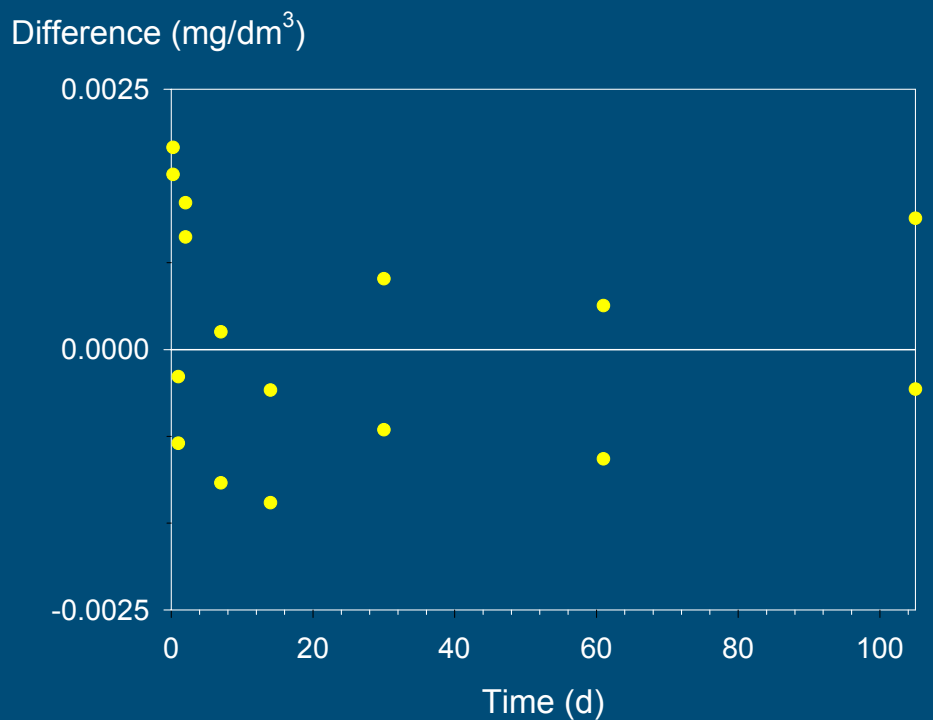




Examples

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





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. ½-2 $K_{oc,soil}$)

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

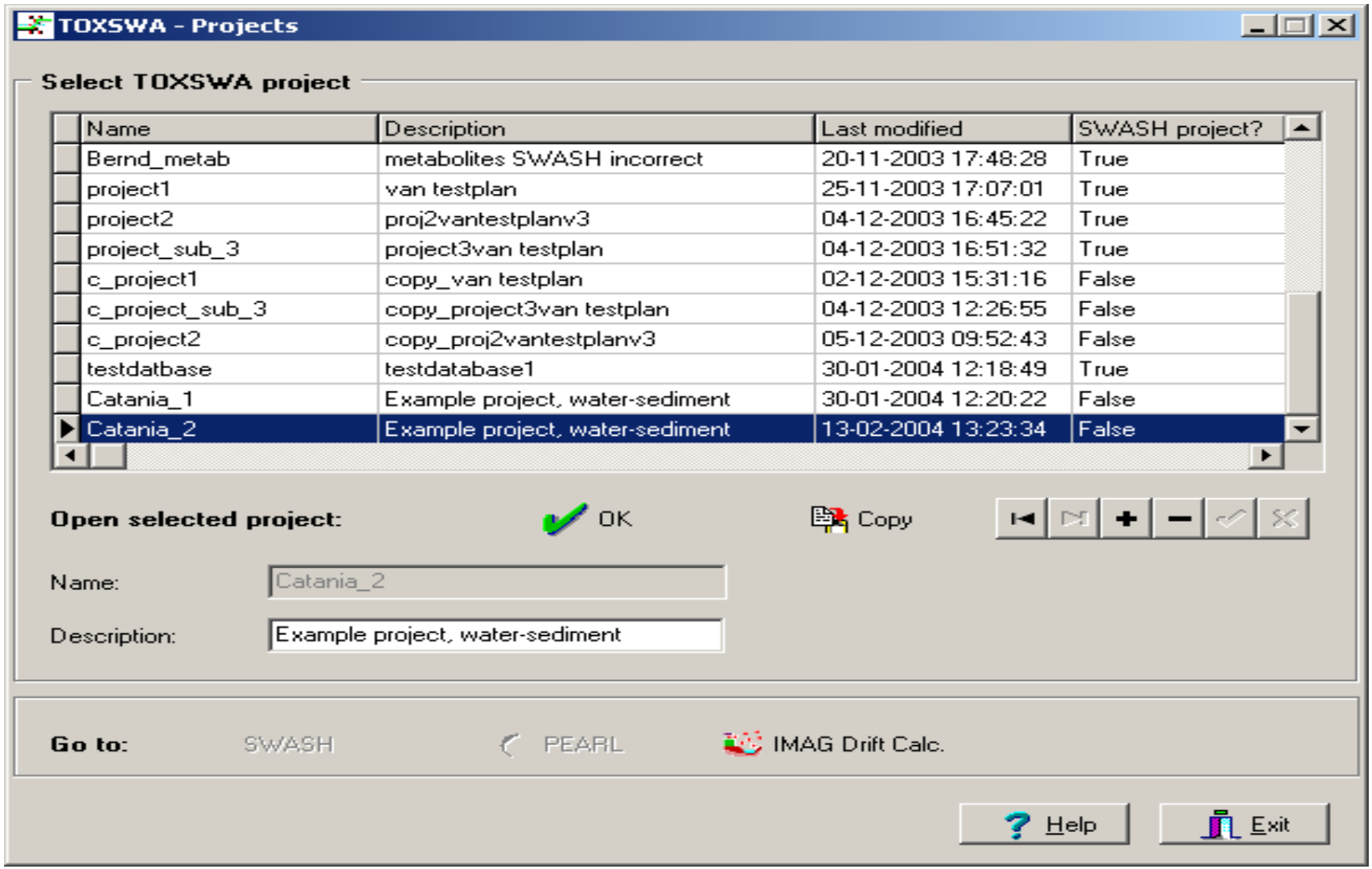
Fitting with TOXSWA

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

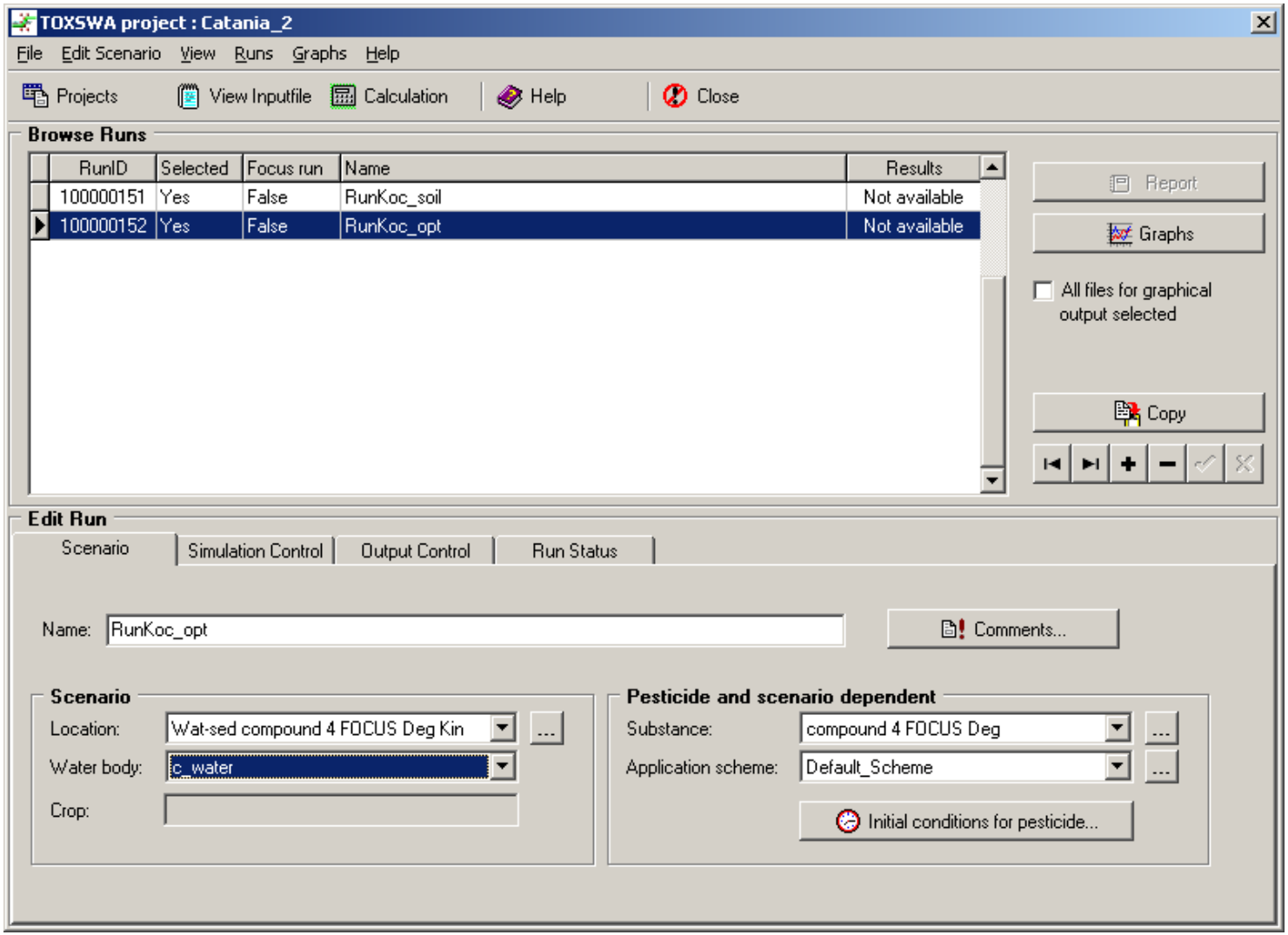
- From summer 2004 in: FOCUS_TOXSWA_2.2.2

  (= FOCUS-TOXSWA_1.1.1 plus
  - current bugs repaired and
  - simulation of water-sediment studies made easier (coupled to PEST))

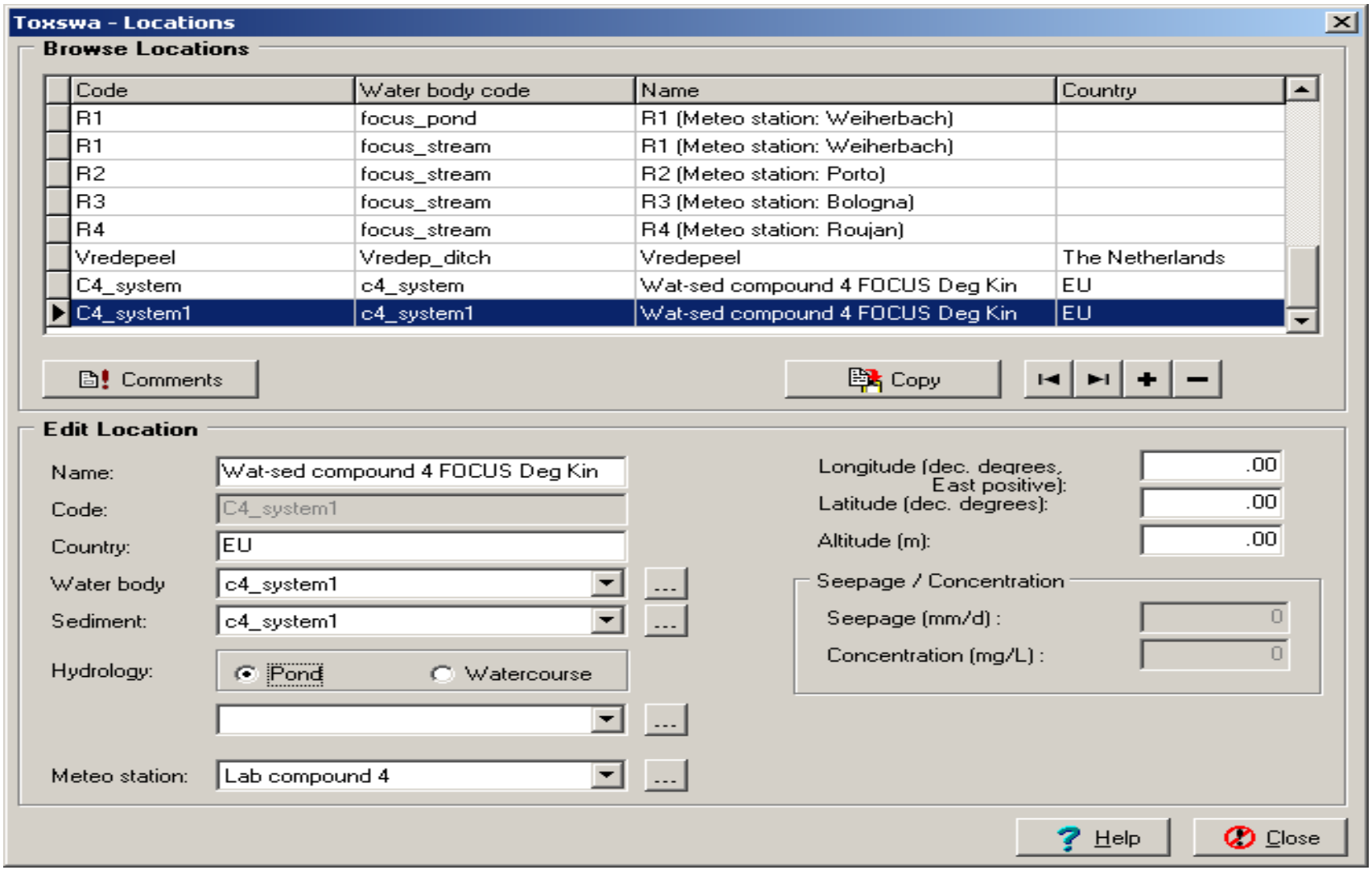
Create project (copy example water-sed)



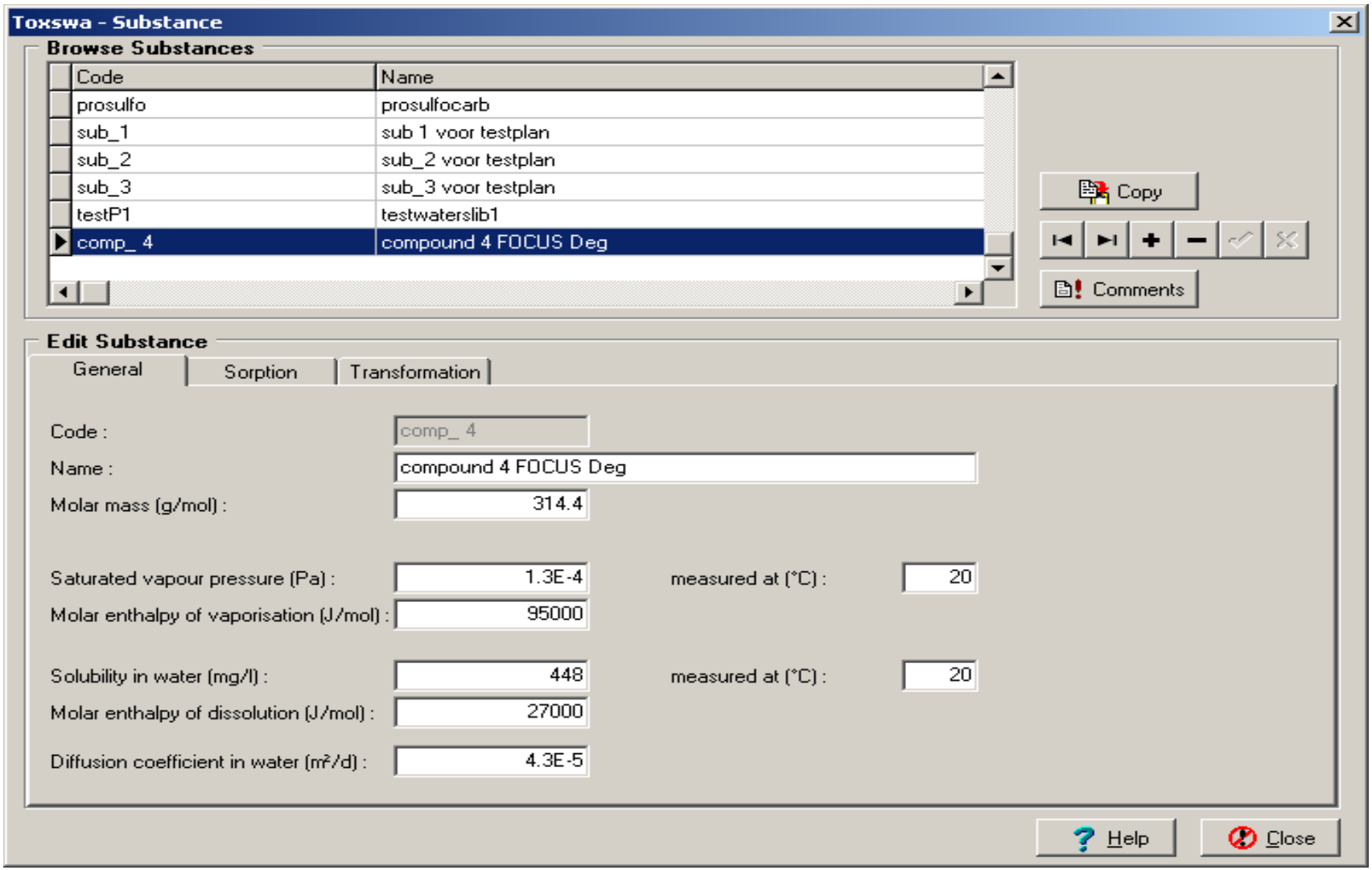
Two runs to optimise



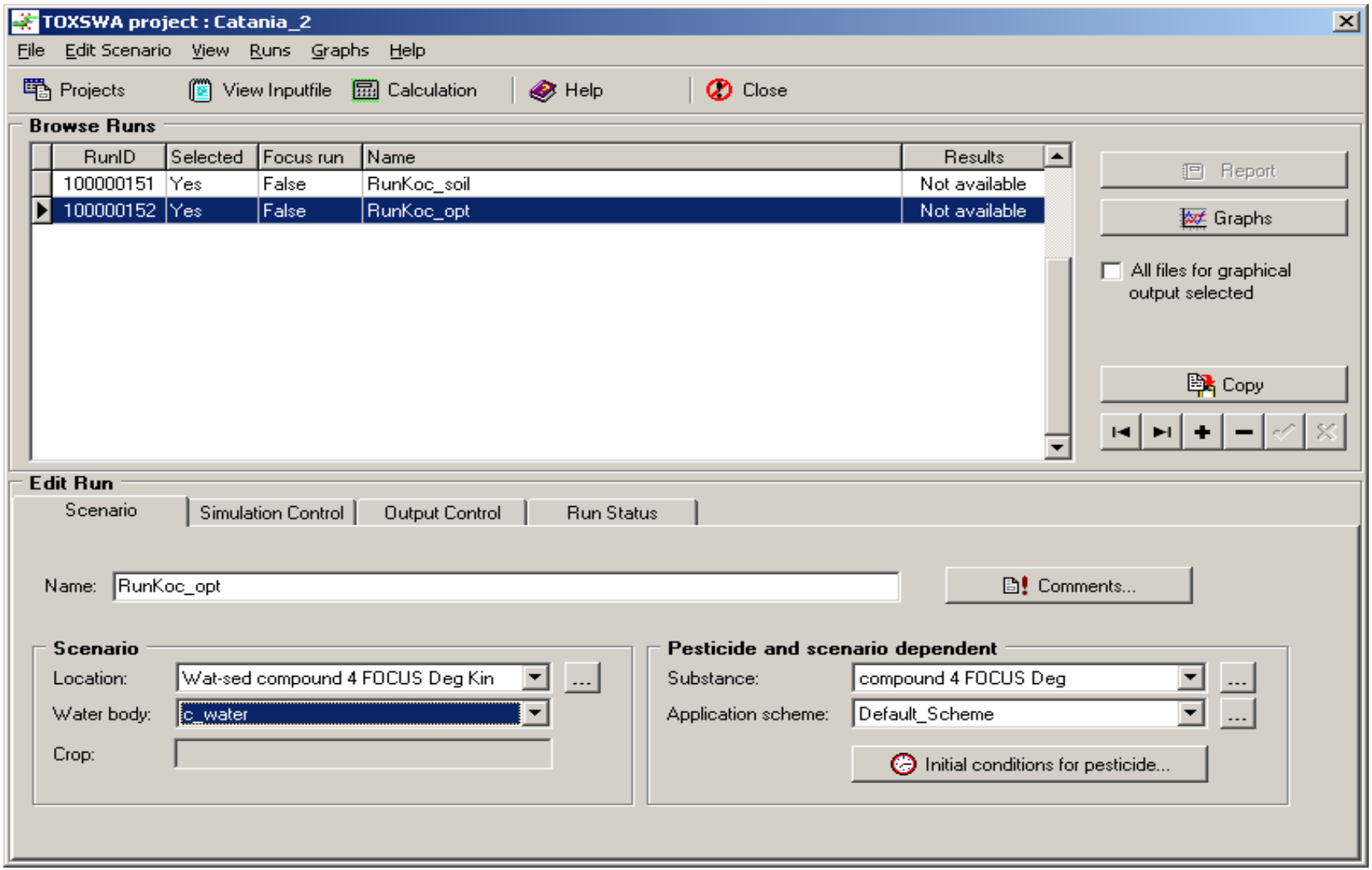
Parameterise system (ca 10 values)



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, $K_{oc,soil} \approx K_{oc,sed}$
    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