

# **Deriving higher tier sorption and degradation parameters from laboratory and outdoor studies**

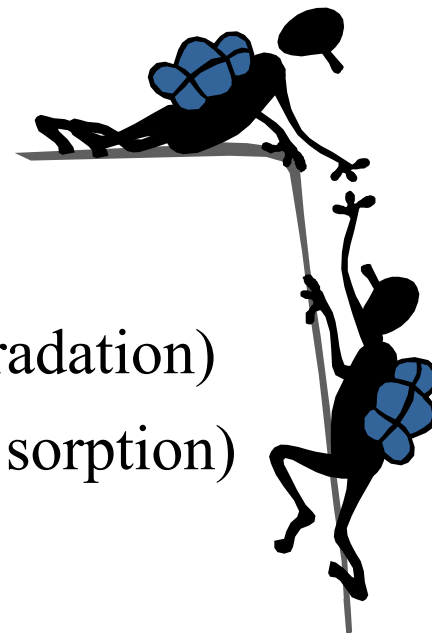
**Bernhard Jene**

## Lower (first) tier parameters ...

- ... result from standard guideline studies (e.g. OECD 106, SETAC)
- ... parameter estimation technique often described in guideline
- ... mostly conservative estimates for the relevant process

## Higher tier parameters ...

- ... require higher tier estimation methods / experiments
- ... are more realistic (less conservative) to describe the relevant processes (e.g. field degradation versus lab. degradation)
- ... are required to describe higher tier processes (e.g. kinetic sorption)



# Higher tier parameters can result from:

## *higher tier evaluation methods of guideline studies*

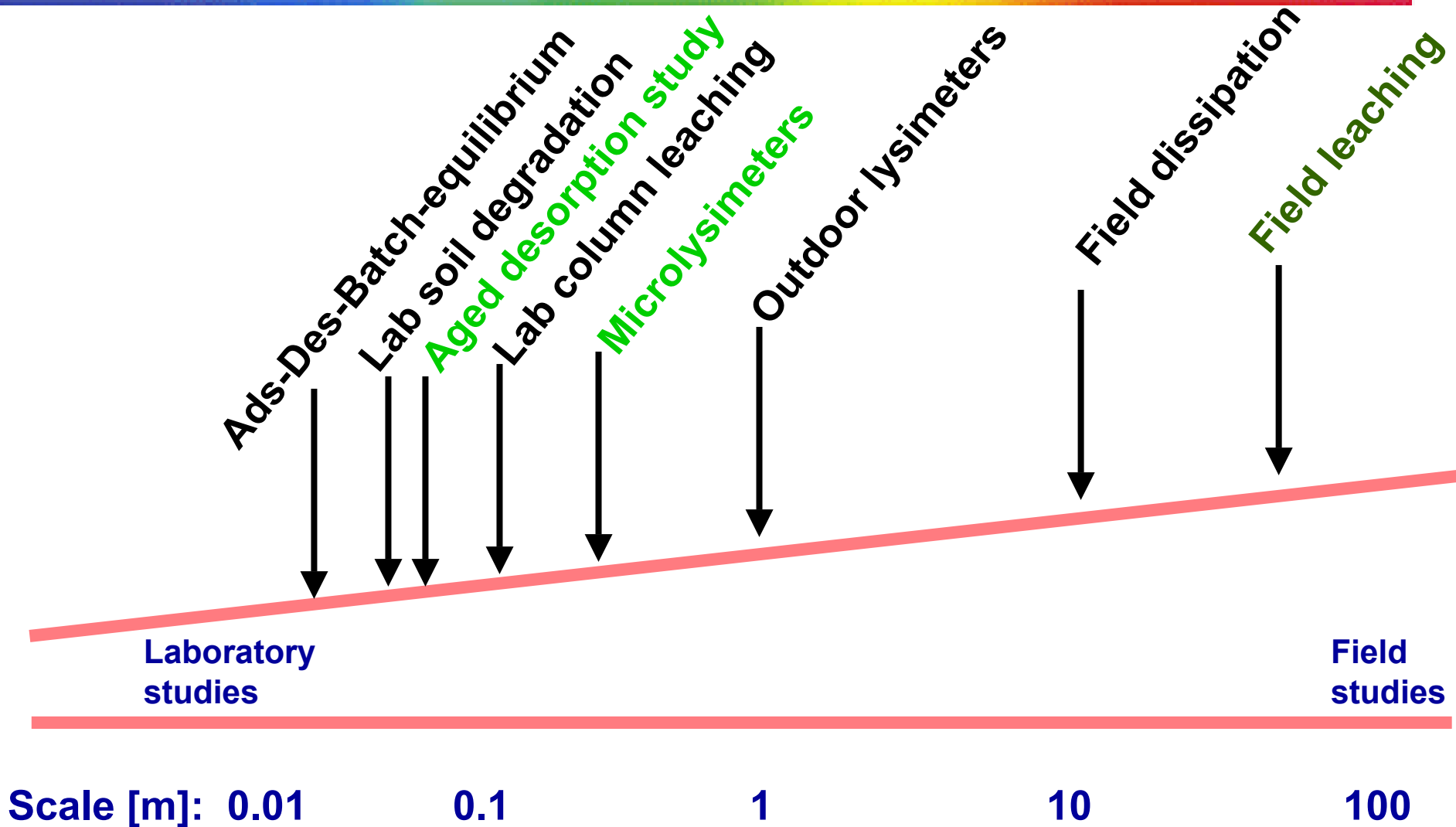
- + availability of studies -> no additional experimental work
- + (regulatory) acceptance of study design
- + maximum use of information from guideline studies
  
- study design is not optimised for parameter estimation  
(parameters sensitivity)
- relevant process may not be included

# Higher tier parameters can result from:

## *higher tier study design*

- + design can be optimised to parameter estimation method (modified standard studies)
  - a given variation/error in measurements results in minimum error in estimated parameter
  - lower correlation – better parameter identification
- + new study type that investigates processes that are not covered by guideline studies
- additional effort – costs
- acceptance of study design often not clear

# Spatial scale of experimental studies



## **Example 1:**

### ***Kinetic parameters from batch equilibrium adsorption desorption study (OECD 106)***

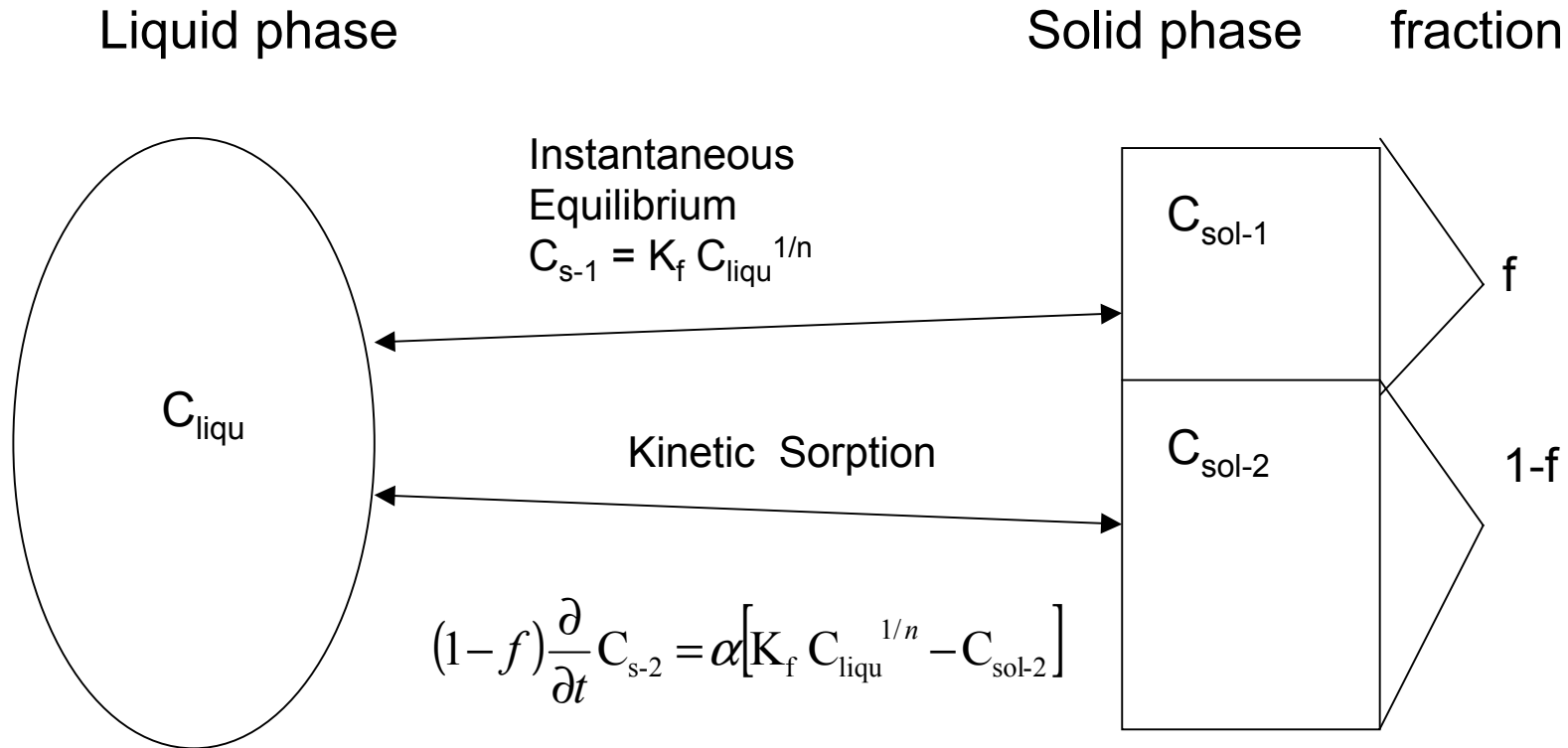
#### **Theory:**

- **sorption hysteresis is expression of non-equilibrium sorption**
- **evaluation of data using a kinetic sorption model  
(FITHYST, Streck et al., 1993)**
- **kinetic sorption parameters can be derived**



# Higher tier evaluation of guideline studies

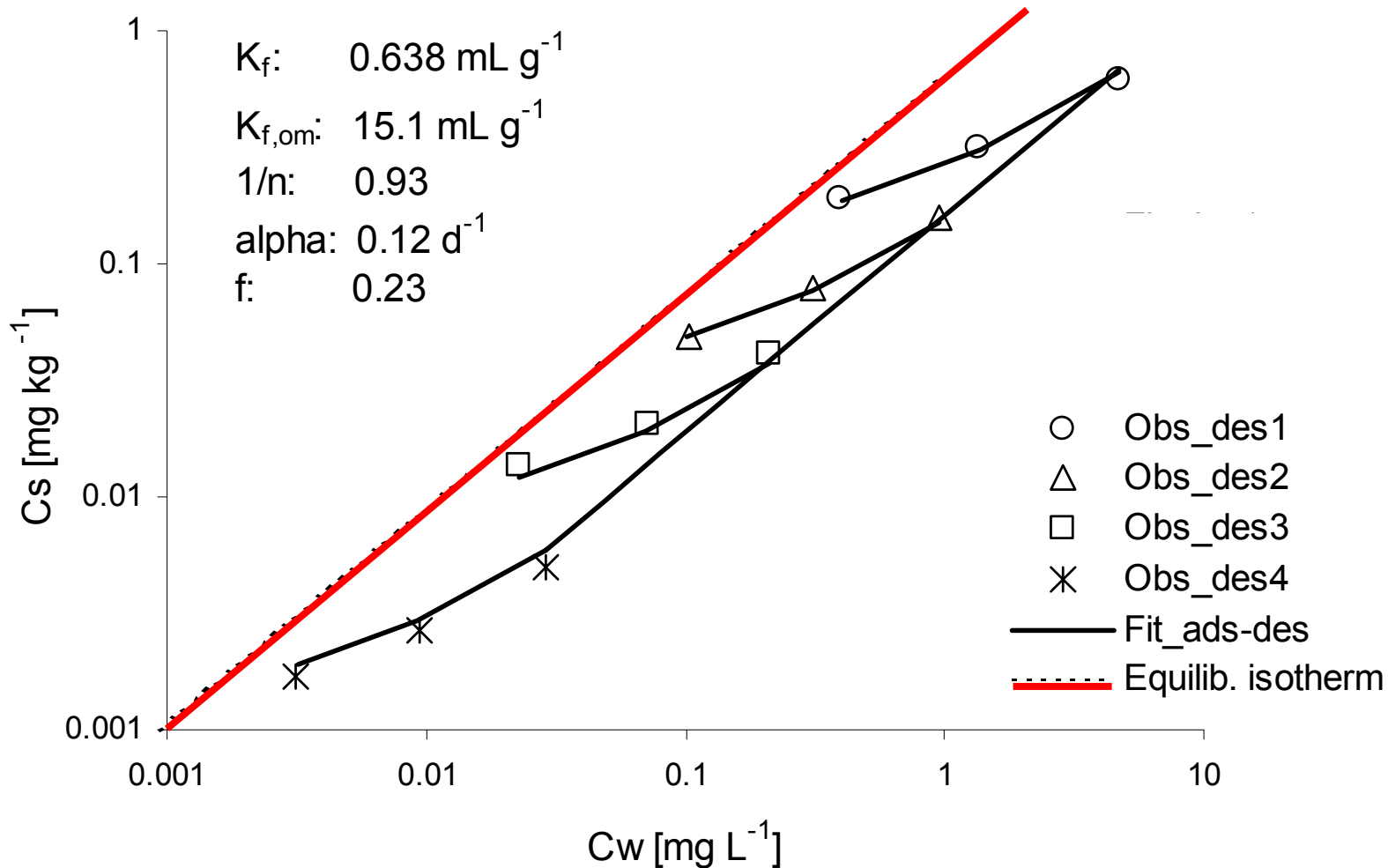
## Example 1: Batch equilibrium adsorption desorption study



(Streck et al, 1993)

# Higher tier evaluation of guideline studies

## Example 1: Batch equilibrium adsorption desorption study



## *Example 1: Batch equilibrium adsorption desorption study*

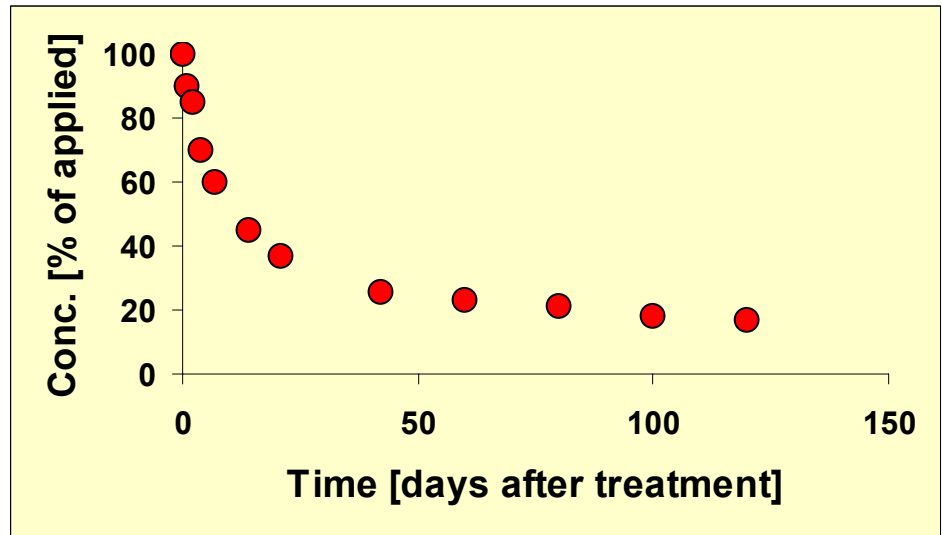
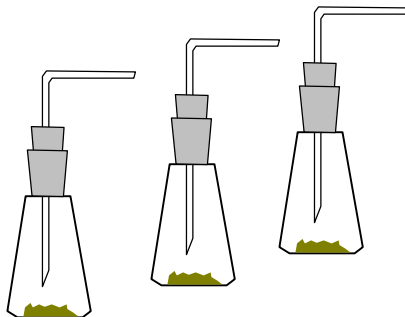
- + **FITHYST makes also use of desorption isotherms**
- + **kinetic parameters for appropriate leaching models can be derived**
- + **no additional non-guideline study necessary**
  
- **at minimum 2 desorption steps necessary (better 3 - 4)**
- **rate parameter might be too high because of shaking of the system (additional kinetic energy)**
- **often close correlation between parameters**

## Example 2: Laboratory soil degradation study (Boesten, FOCUS kinetics report)

### Theory:

- bi-phasic behaviour of degradation curve is expression of kinetic sorption -> no degradation in non-equilibrium phase
- parameters of biphasic model (DFOP or SFORB) can be transformed to kinetic sorption model

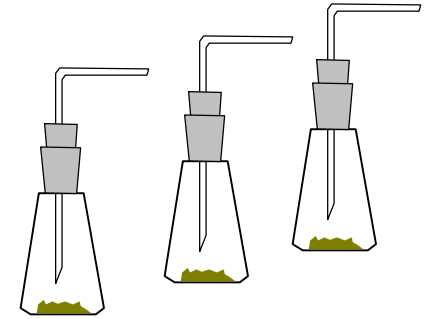
$$M(t) = M_0(g e^{-k_1 t} + (1-g) e^{-k_2 t})$$



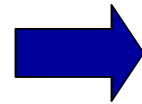
# Higher tier evaluation of guideline studies

## Example 2: Laboratory soil degradation study

$$M(t) = M_0(g e^{-k_1 t} + (1-g) e^{-k_2 t})$$

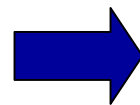


$$k_d = \frac{k_1 k_2}{g k_1 + (1-g) k_2}$$



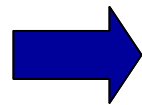
**Desorption rate in PEARL**

$$k_t = g k_1 + (1-g) k_2$$



**Degradation rate in PEARL**

$$\Phi = \frac{g(1-g)(k_1 - k_2)^2}{k_1 k_2}$$

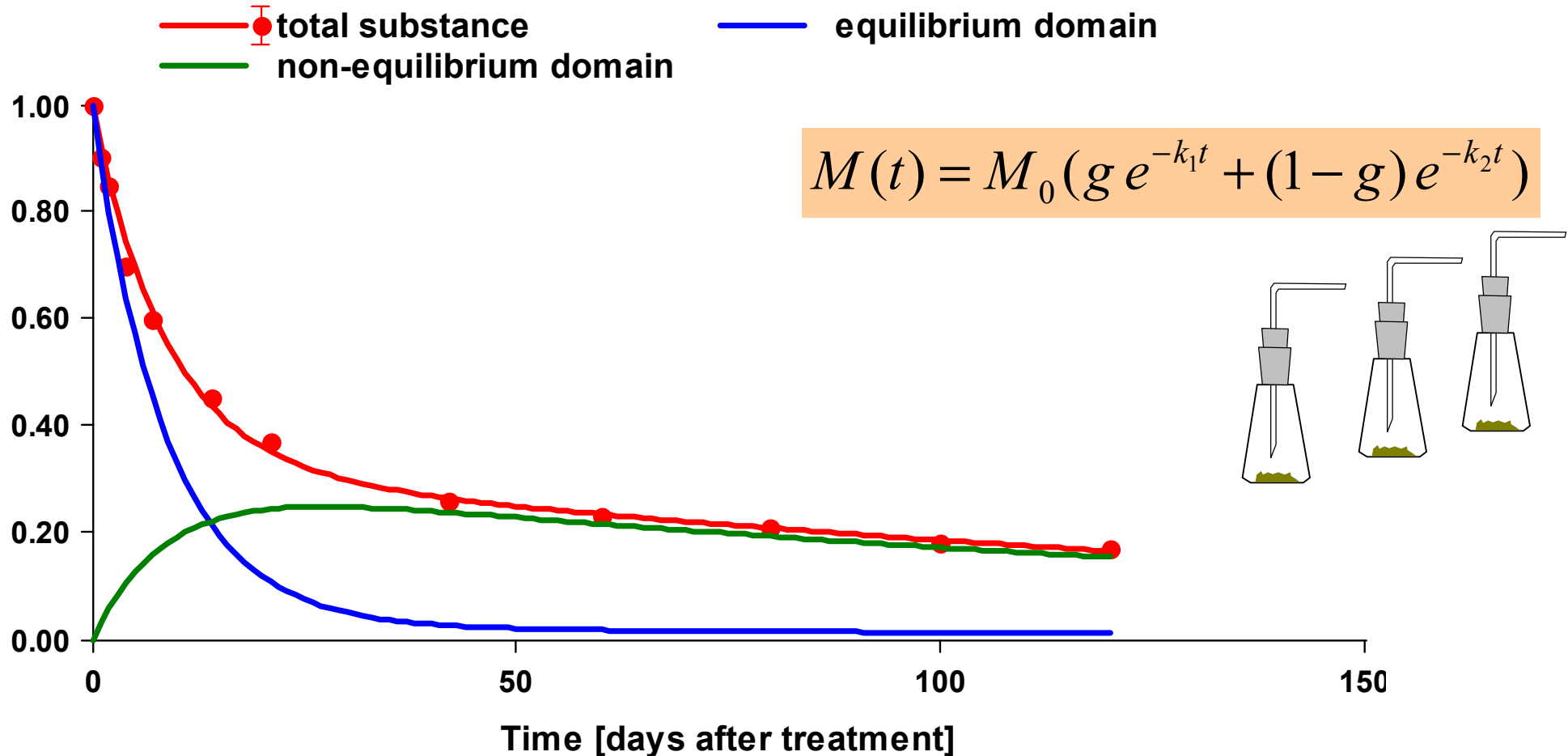


$$f_{NE} = \Phi \frac{\theta + \rho K_{L,EQ}}{\rho K_{L,EQ}}$$

**Fraction of non-linear sorption in PEARL**

# Higher tier evaluation of guideline studies

## Example 2: Laboratory soil degradation study



## *Example 2: Laboratory soil degradation study*

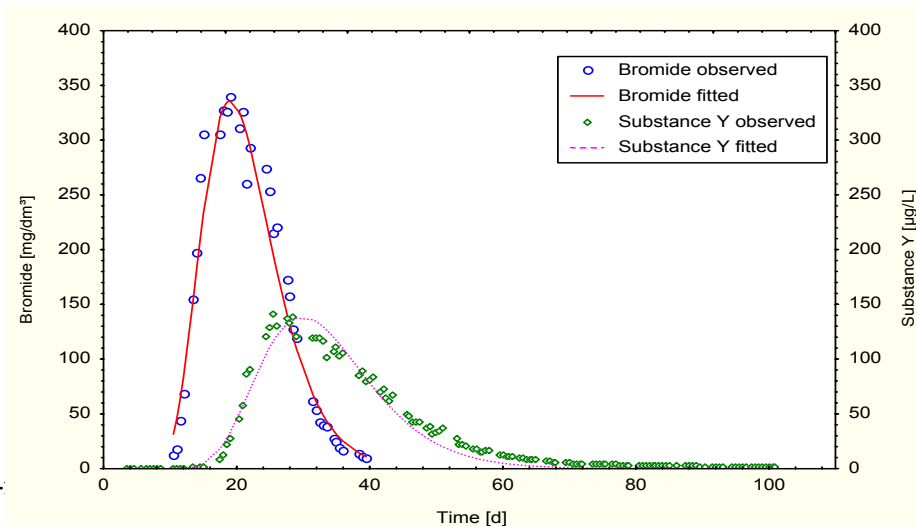
- + Kinetic parameters for appropriate leaching models can be derived
- + No additional non-guideline study necessary
- Limitations with regard to the parameters:
  - $k_d = 0.002 - 0.1 \text{ d}^{-1}$
  - $f_{NE} = 0.1 - 1$
- Correlation between parameters

# Higher tier evaluation of guideline studies

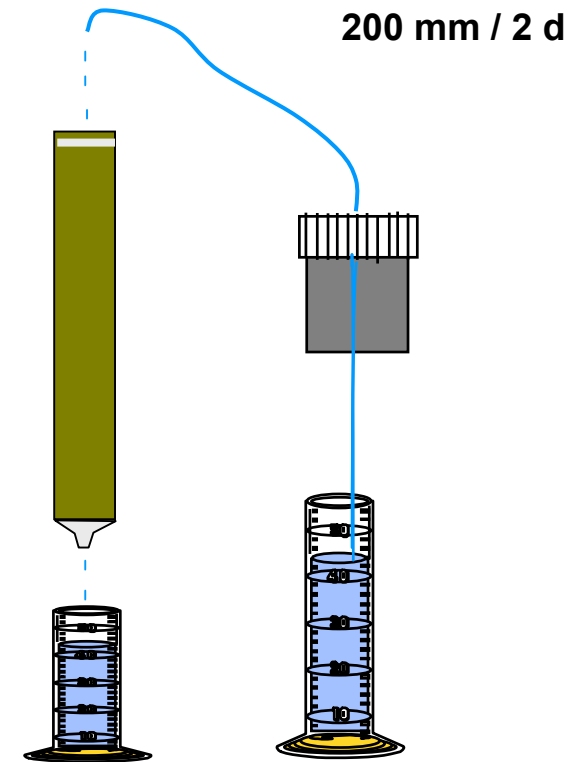
## Example 3: Soil column (aged residues) studies

- + Evaluation of BTC using an appropriate tool (e.g. CXTFIT or numerical model - guidance paper from NL, RIVM)
- + Derivation of (kinetic) sorption parameters

- extremely high pore water velocity
- low fraction of non-equilibrium sorption
- reliability of parameters not clear



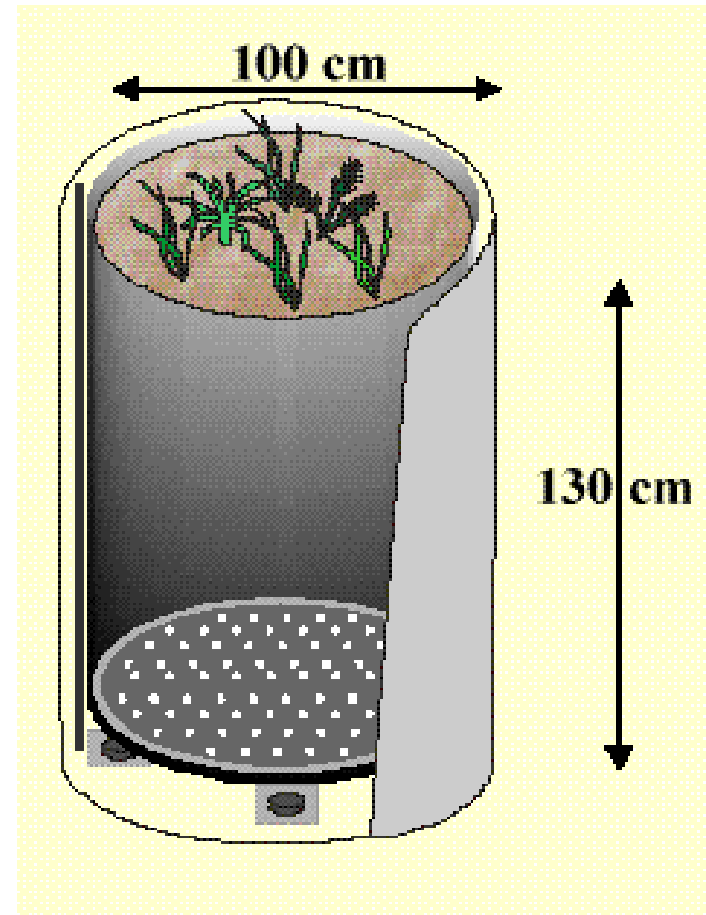
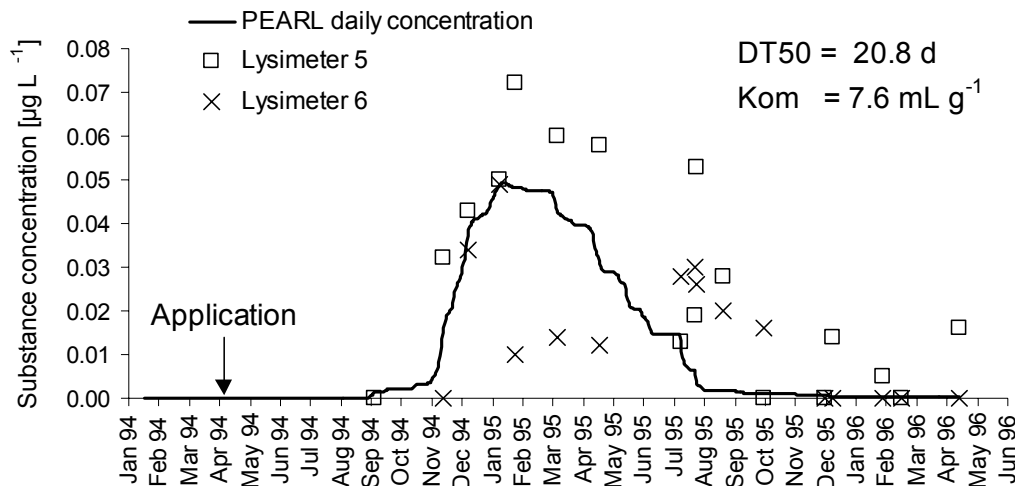
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## Example 4: Inverse modelling of outdoor lysimeter studies

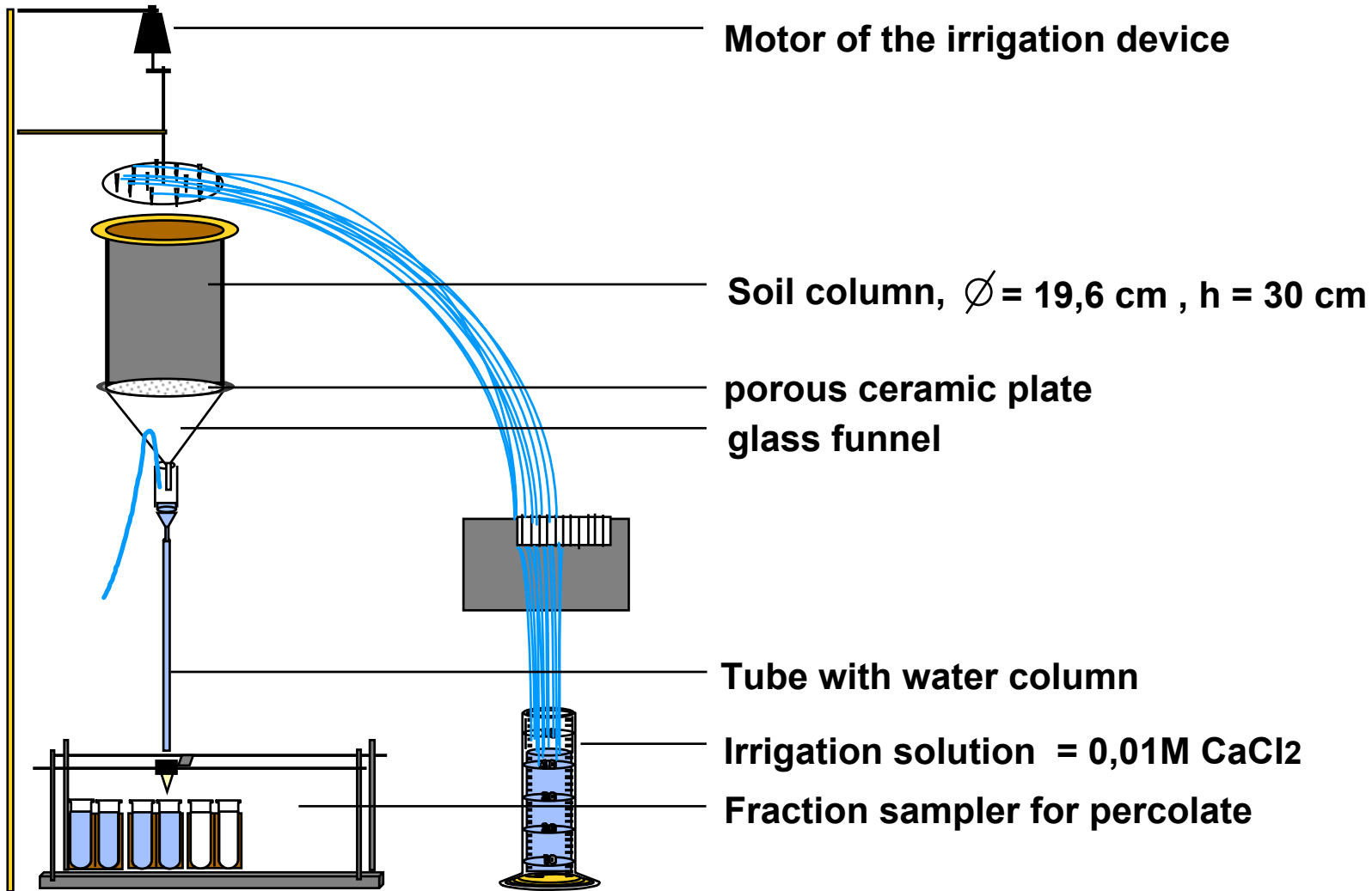
- evaluation of water outflow (ETact)
- evaluation of BTC
- high number of influencing variables



## *Further methods: Inverse parameter estimation*

- **Temperature and moisture normalised degradation rates from field dissipation studies**
- **Degradation and sorption parameters from field dissipation/leaching studies**

# Higher tier studies: Microlysimeter

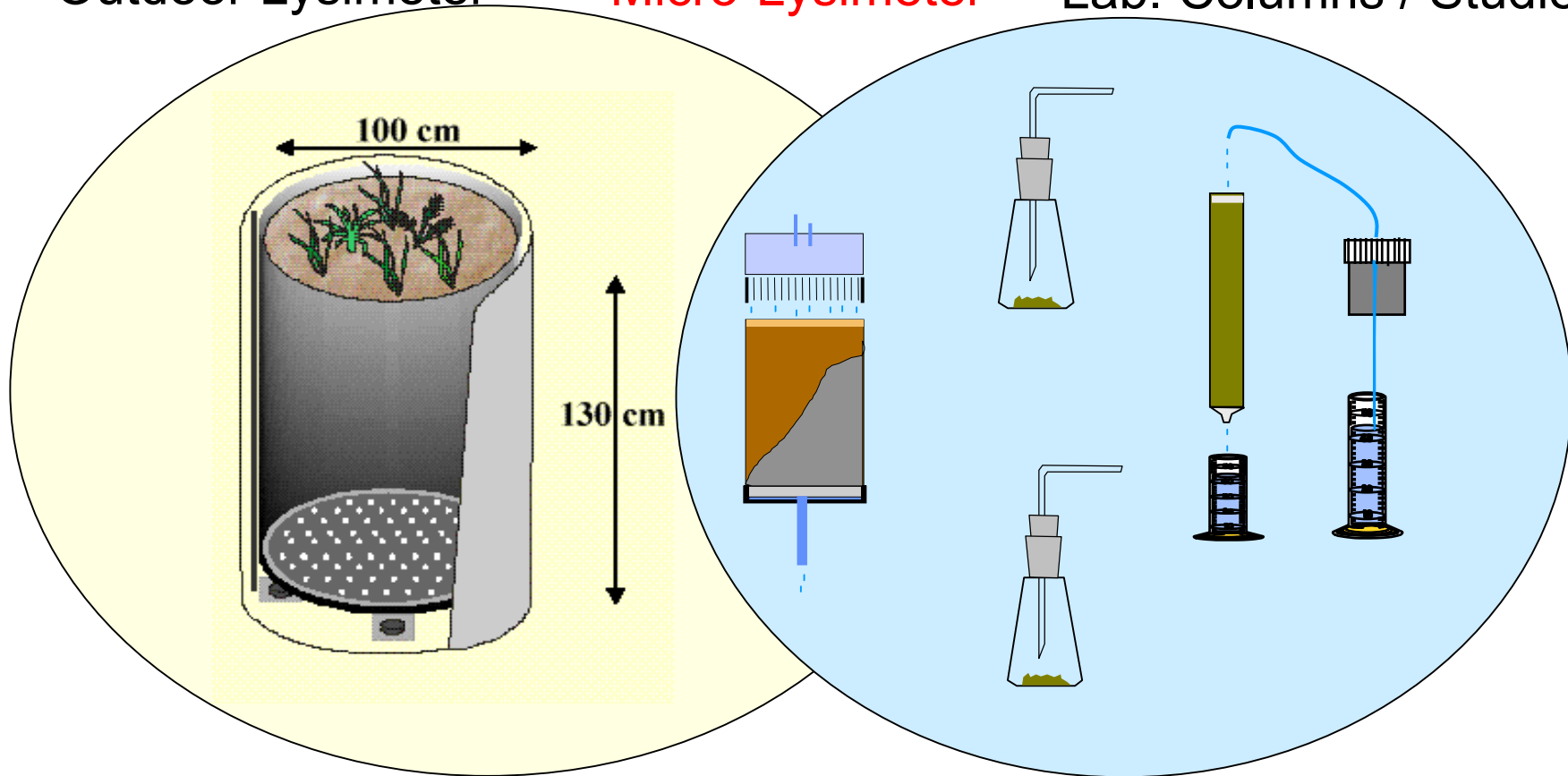


# Higher tier studies: Microlysimeter

Outdoor Lysimeter

Micro-Lysimeter

Lab. Columns / Studies

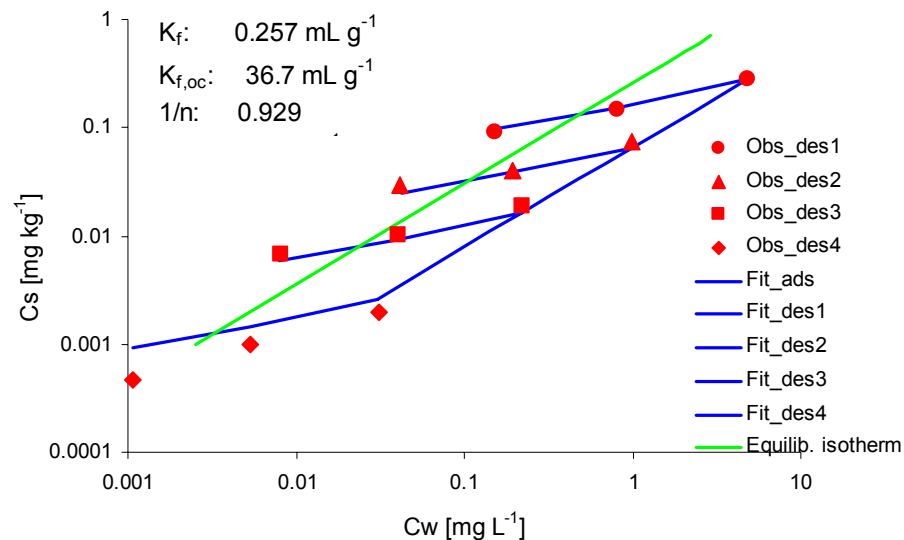
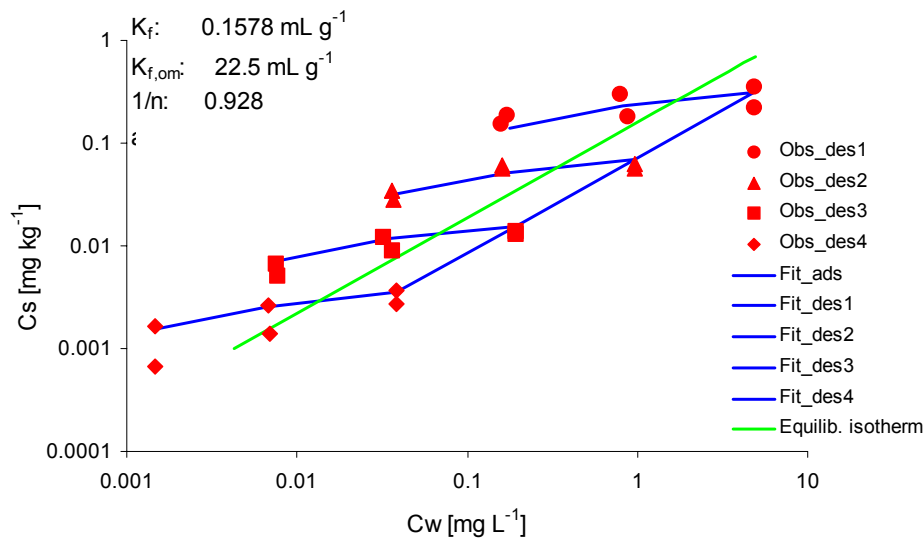


- Controlled conditions
- Optimisation of boundary conditions (ECOPLAN) → reliable parameters

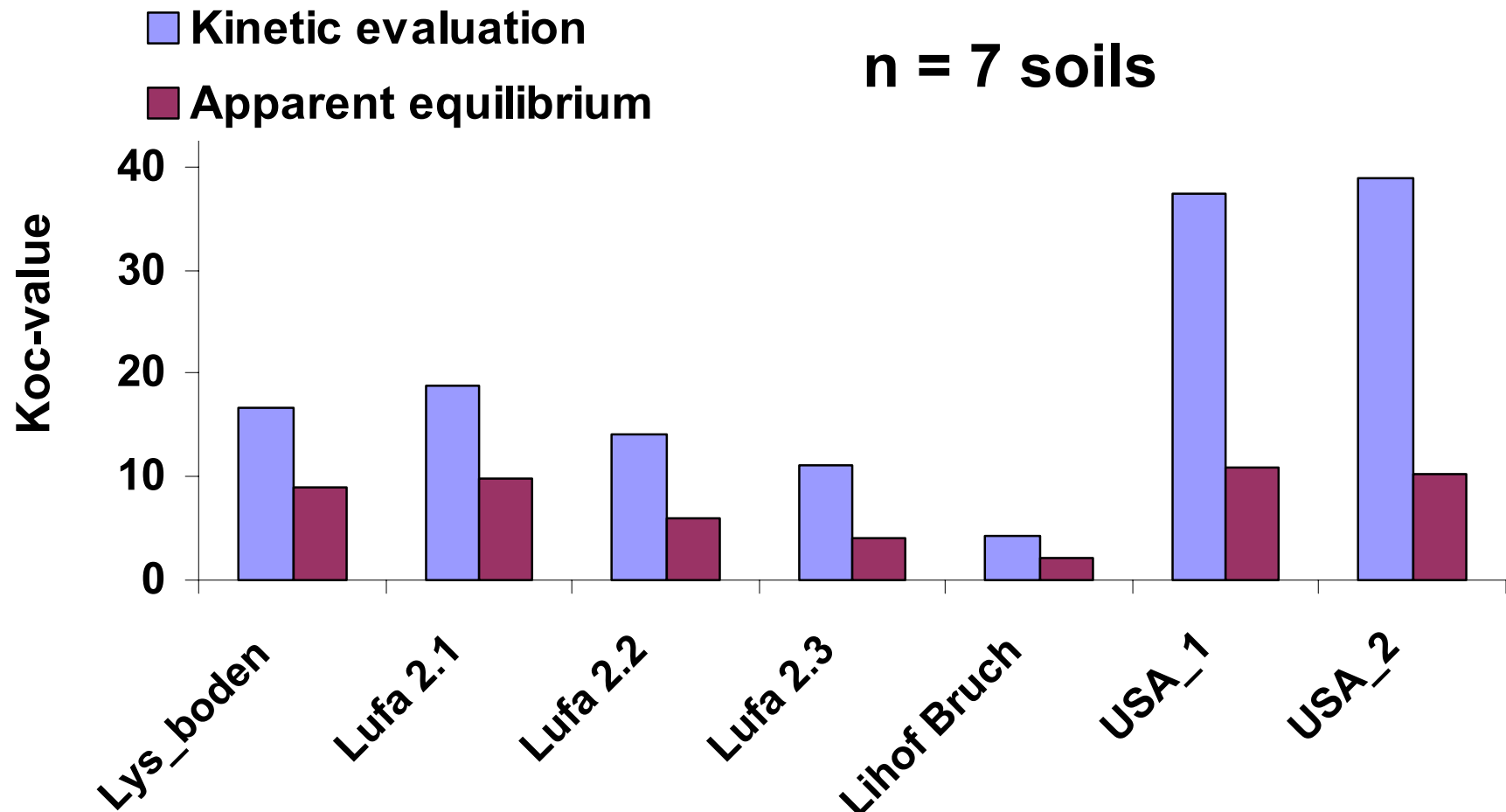
# **Case study: higher tier sorption parameters**

**An integrated multi-factorial approach  
to derive higher tier sorption parameters from  
guideline studies**

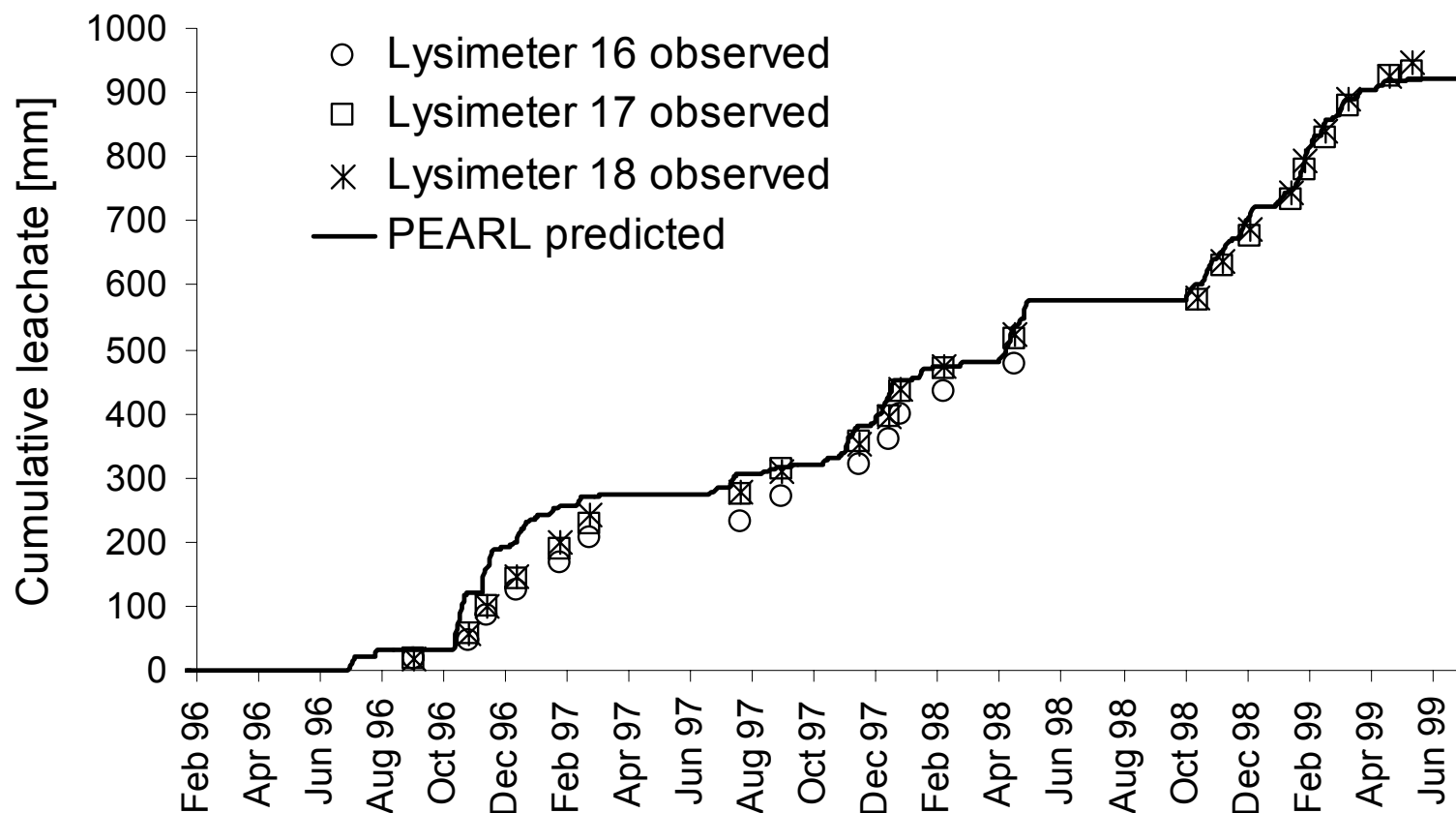
## Part 1: evaluation of ads-des OECD 106 studies



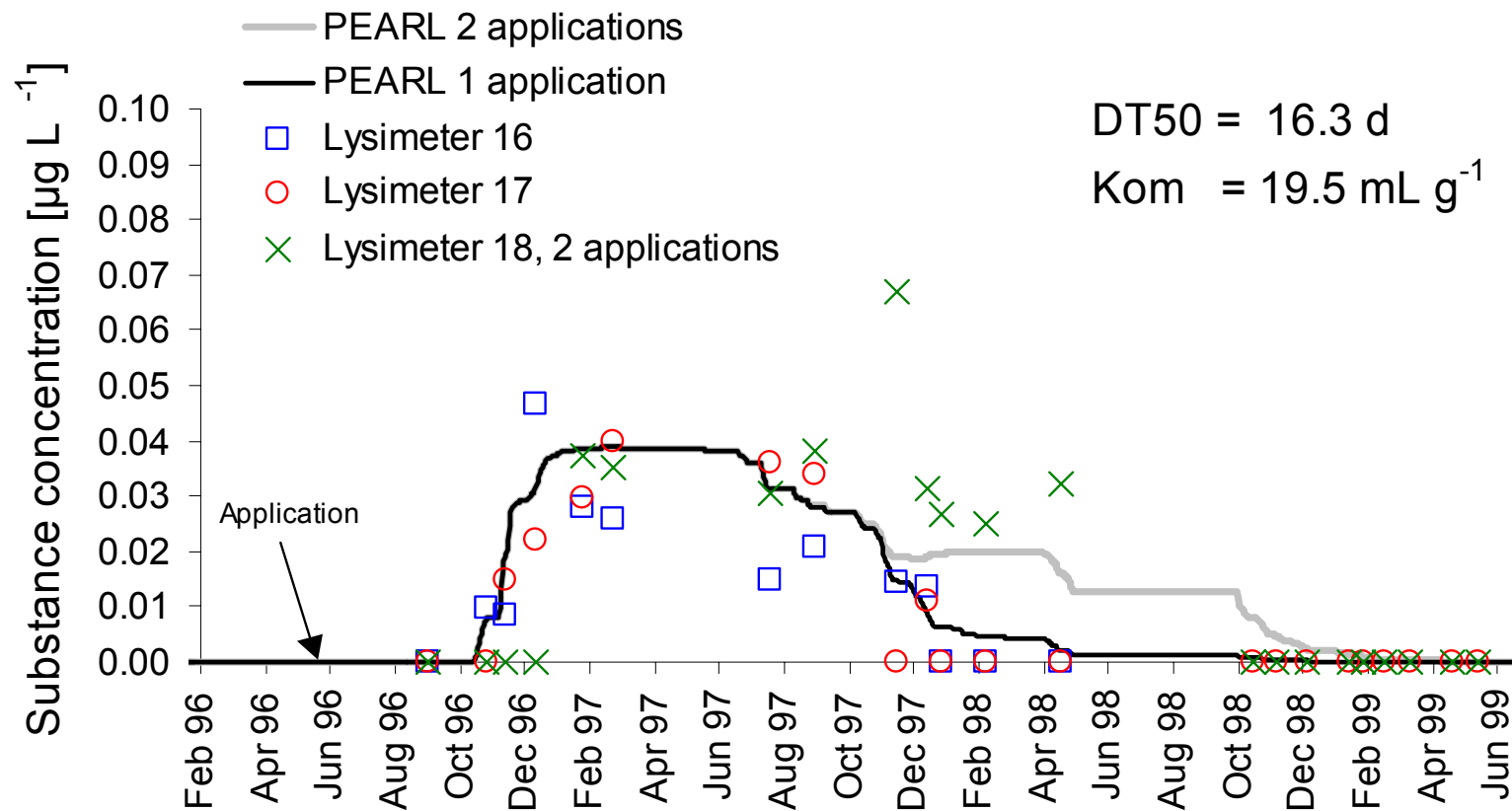
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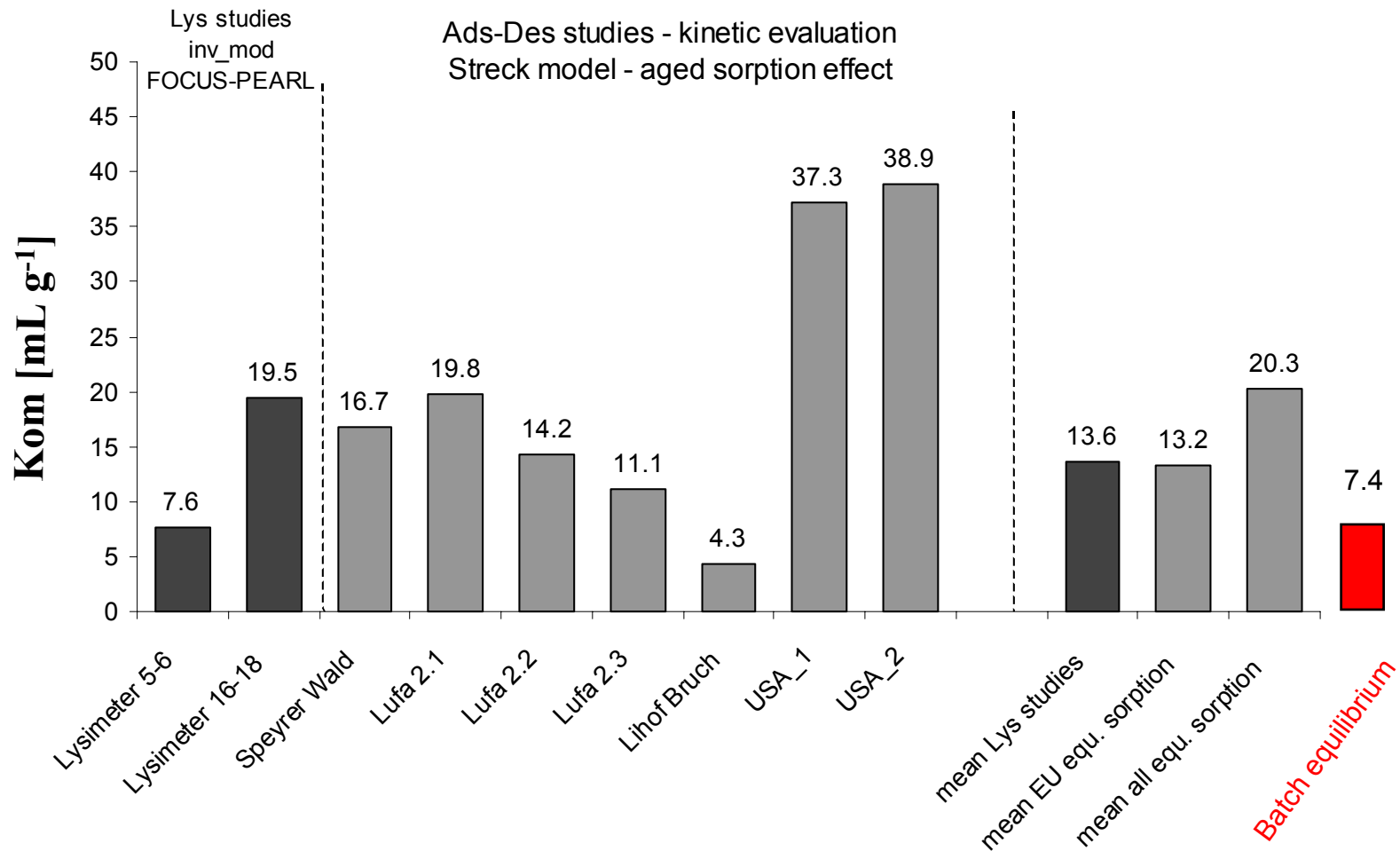
## Part 2: inverse modelling of lysimeter studies (n = 5 lysimeter)



## Part 2: inverse modelling of lysimeter studies



# Case study: higher tier sorption



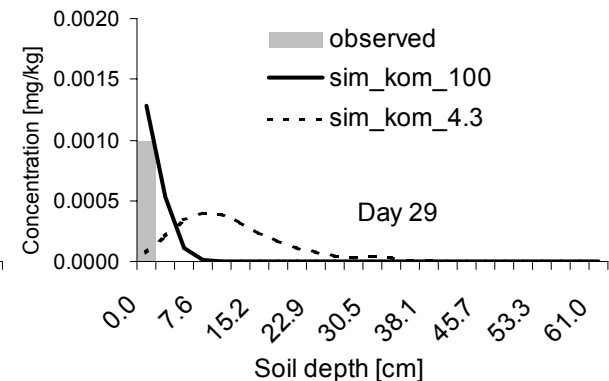
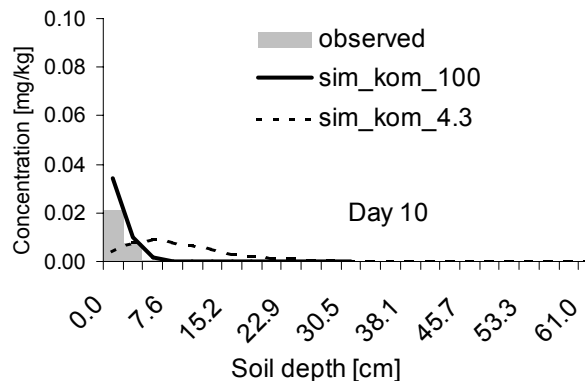
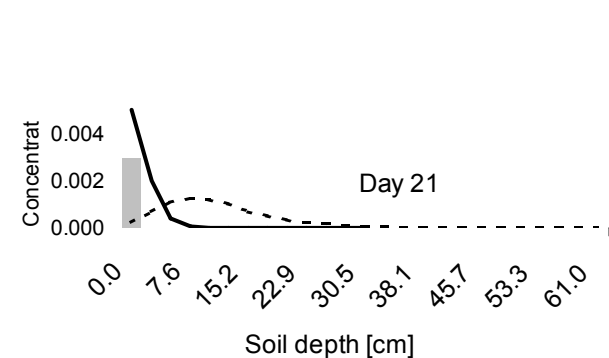
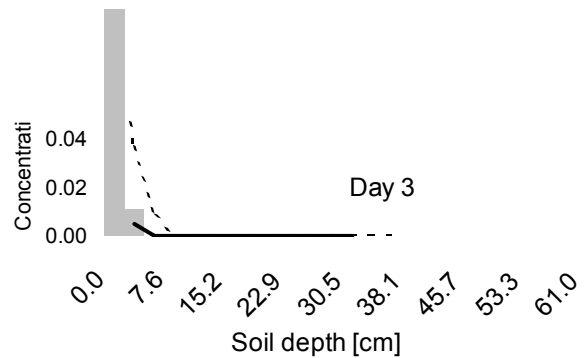
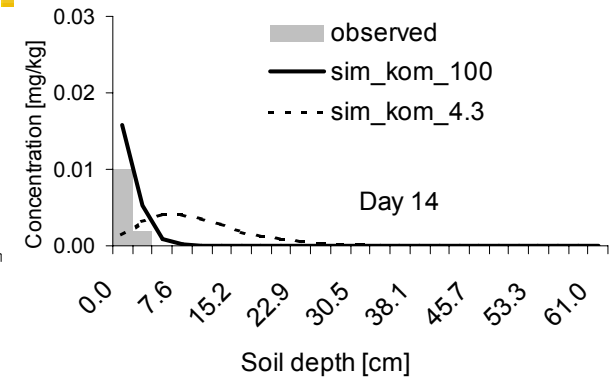
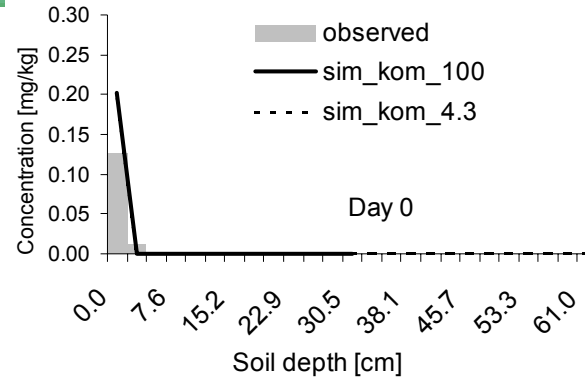
## ***Part 3: evaluation of field dissipation studies (reality check)***

- > 10 experimental sites
- > forward calculation with different  $K_{om}$ -values (sensitivity analysis) using site specific soil and weather data
- > qualitative assessment of actual sorption behaviour
- > visual assessment of experimental data versus simulation

# Case study: higher tier sorption

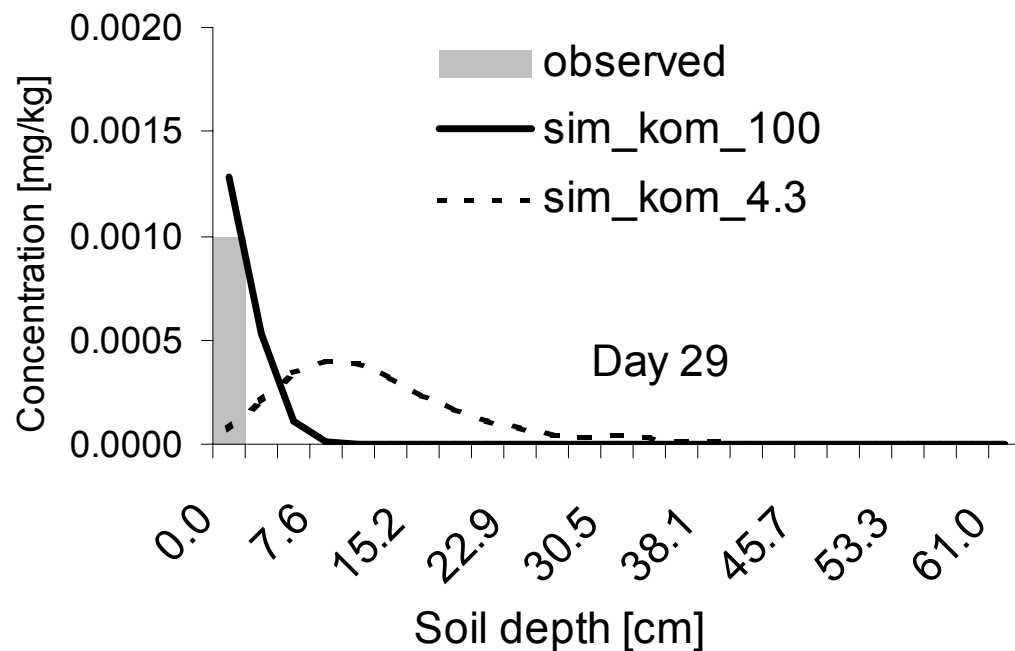
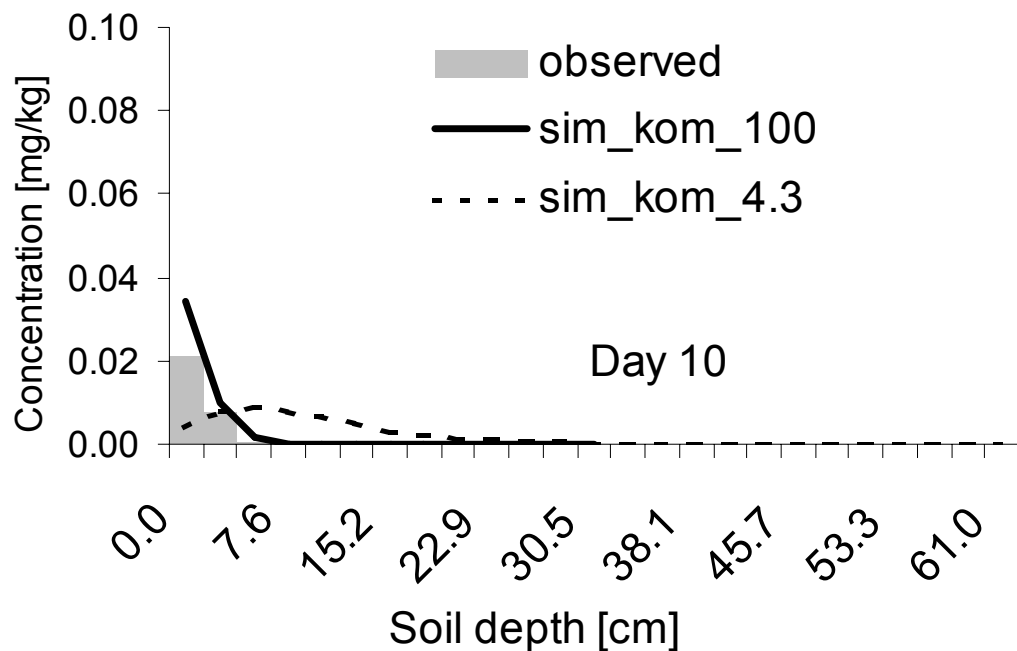


## Part 3: evaluation of field studies (10 sites)



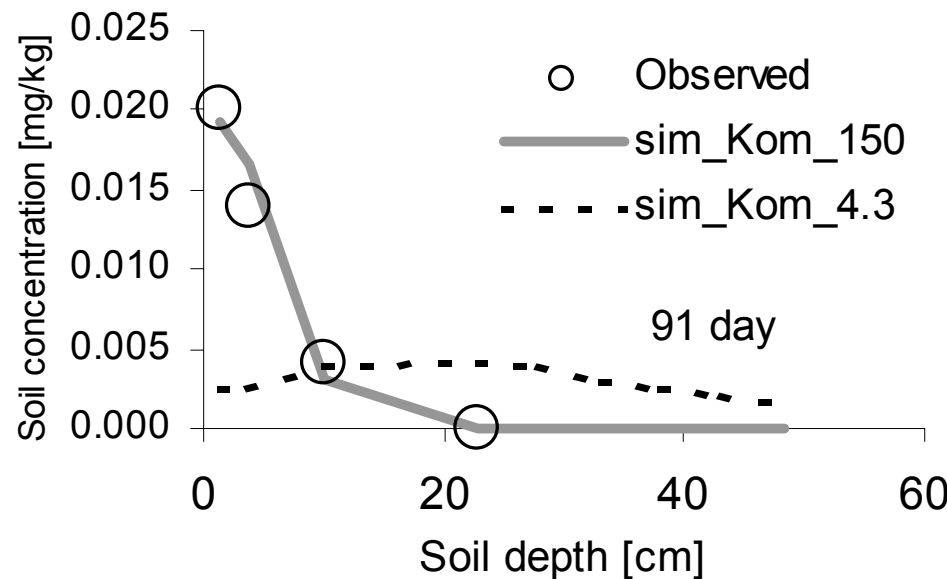
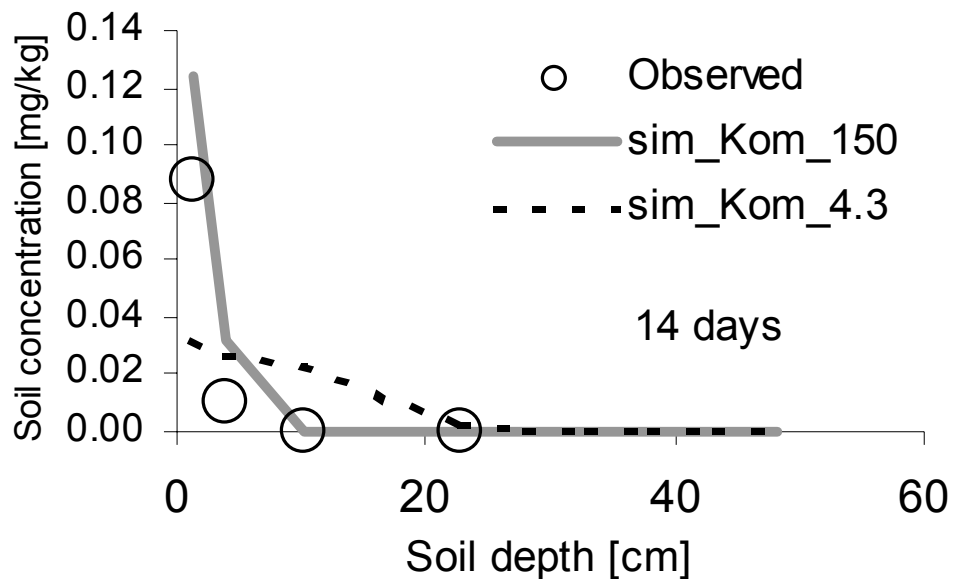
## Part 3: evaluation of field studies (10 sites)

### PEARL 1.1.1



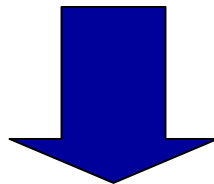
## Part 3: evaluation of field studies (10 sites)

### PEARL 1.1.1



## *Part 3: evaluation of field studies (results)*

- An agreement between simulated and observed concentrations could be achieved by using increased sorption values
- Using the apparent equilibrium  $K_{om}$  from ads-des studies leads to a clear overestimation of the leaching



*The higher tier evaluation of all experimental parts showed that the actual sorption of the compound was underestimated by the apparent  $K_{om}$  of the ads-des batch-equilibrium experiments*

## higher tier evaluation of guideline studies can...

- ... be carried out without additional experimental data (only additional evaluation work)
- ... help to obtain more realistic (less conservative) parameters
- ... can be an important tool for process identification
- ... can help to obtain a comprehensive consistent picture about the e-fate behaviour of a substance