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

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Some kind of definition…

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Lower (first) tier parameters …

… result from standard guideline studies (e.g. OECD 106, SETAC)

… parameter estimation technique often described in guideline

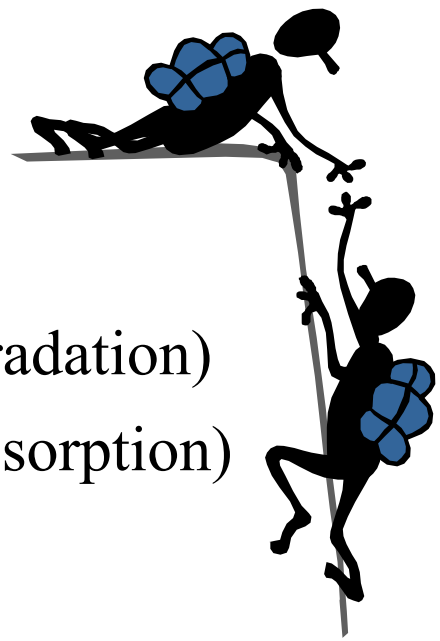
… mostly conservative estimates for the relevant process

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)



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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

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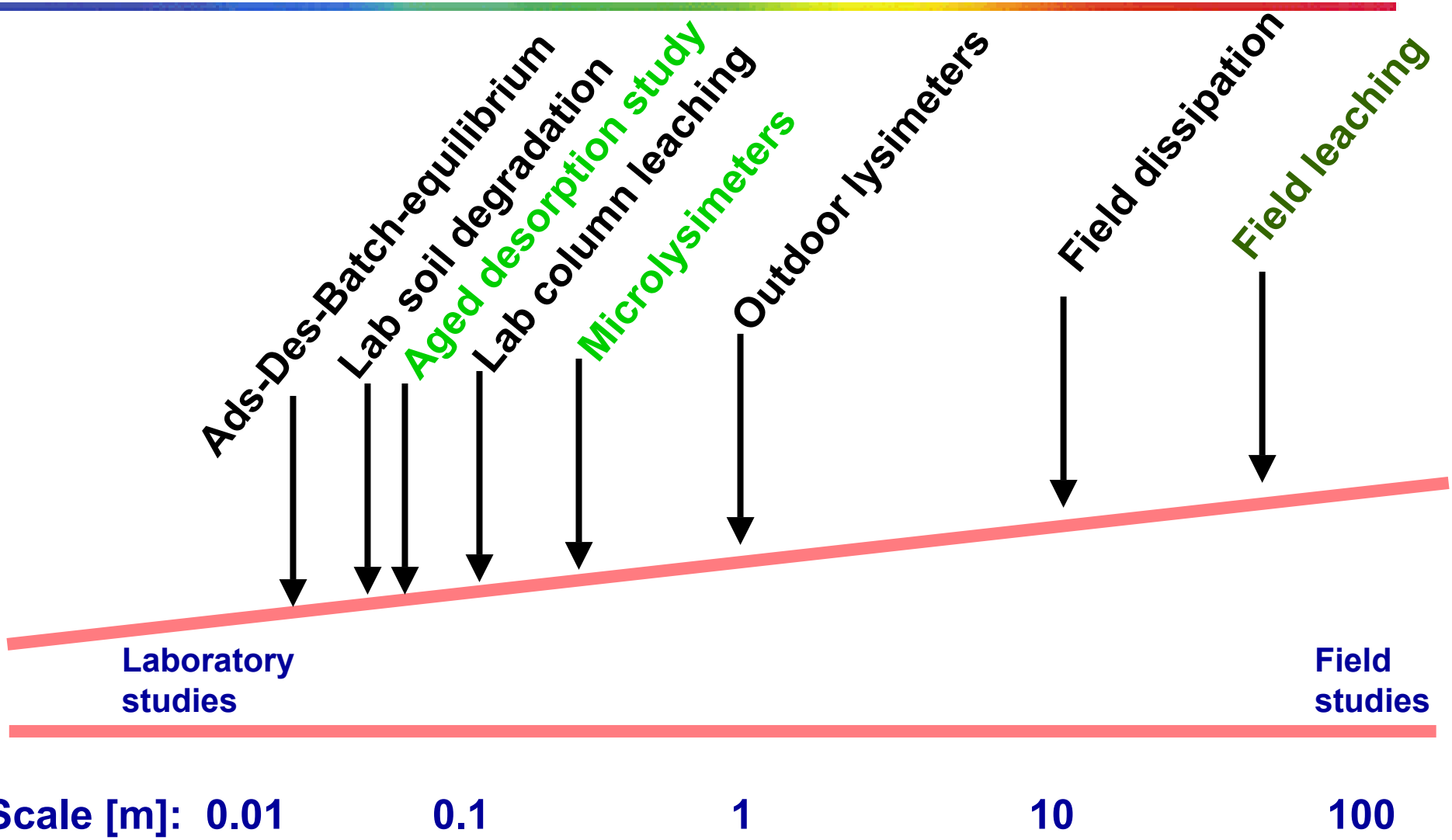
Higher tier parameters can result from:

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



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Higher tier evaluation of guideline studies

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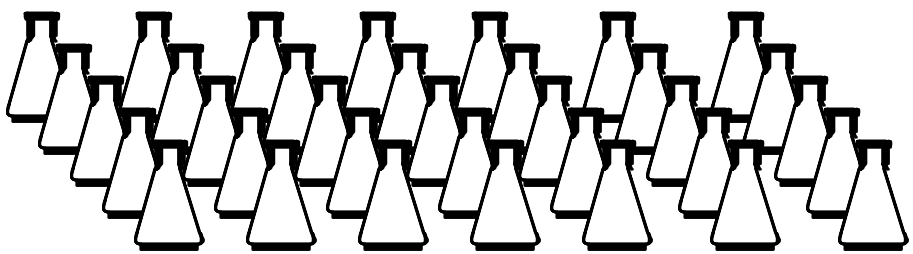
Example 1:
Kinetic parameters from batch equilibrium adsorption desorption study (OECD 106)

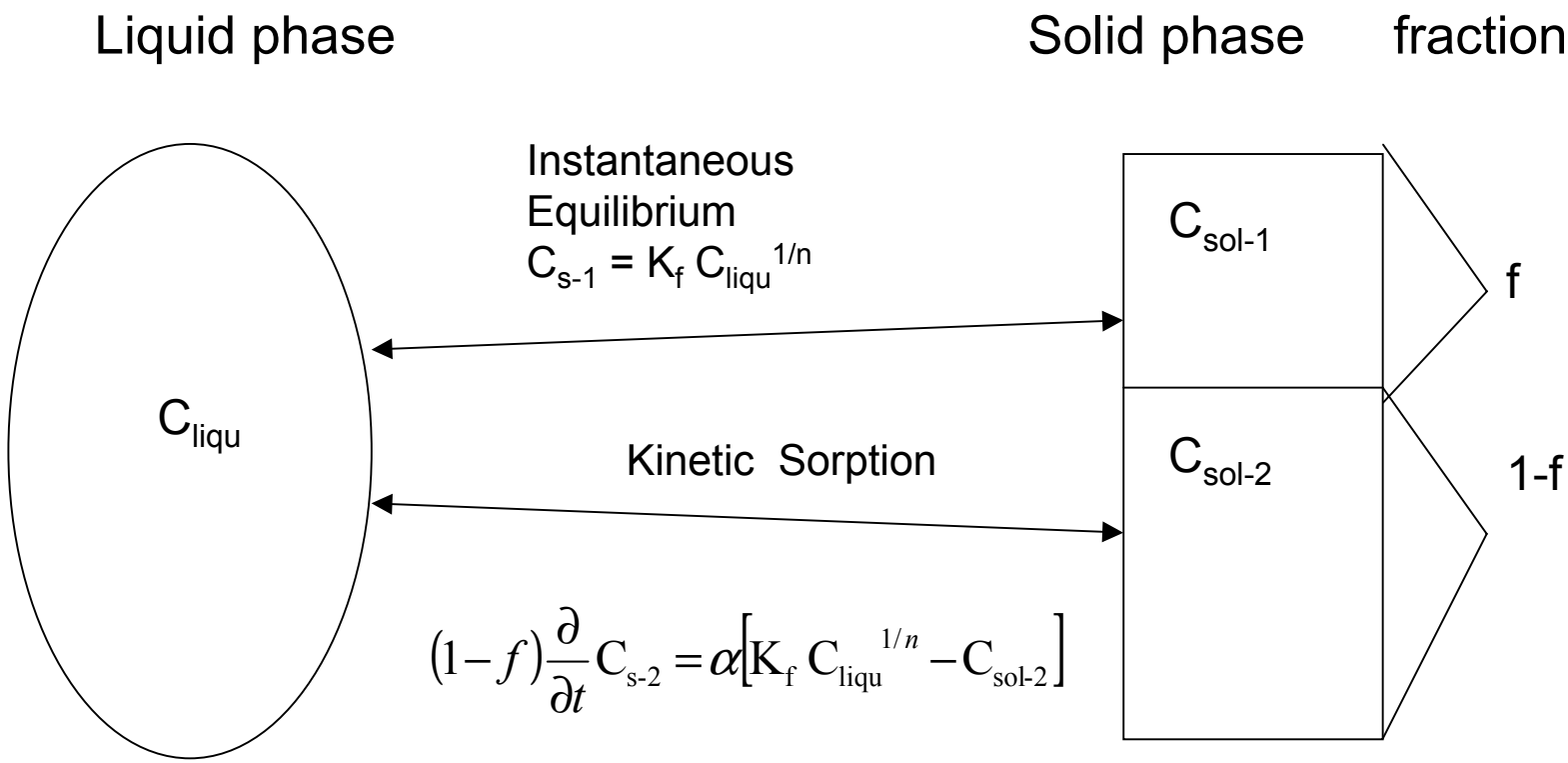
Theory:

- **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)

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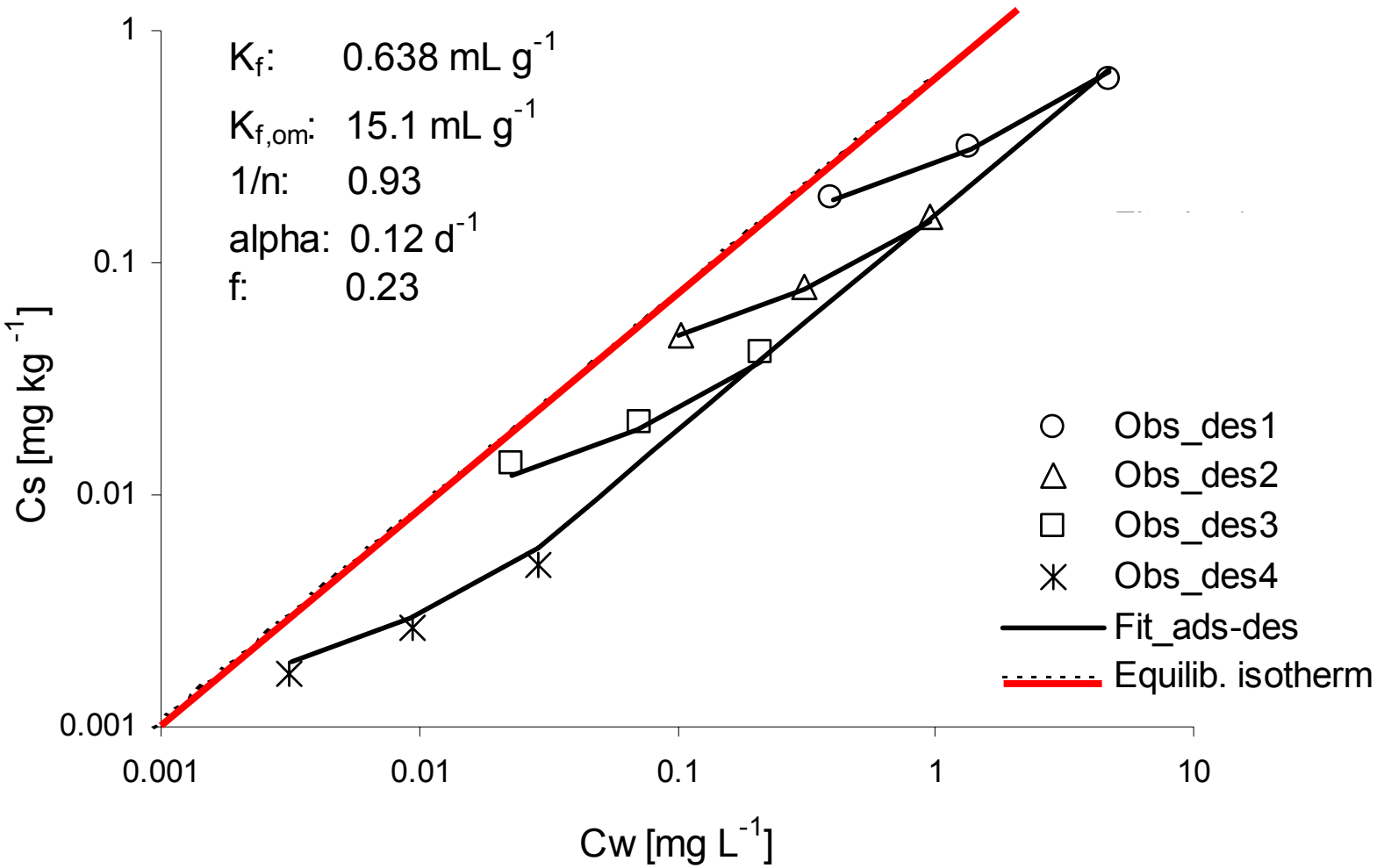
Higher tier evaluation of guideline studies

Example 1: Batch equilibrium adsorption desorption study



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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

Higher tier evaluation of guideline studies

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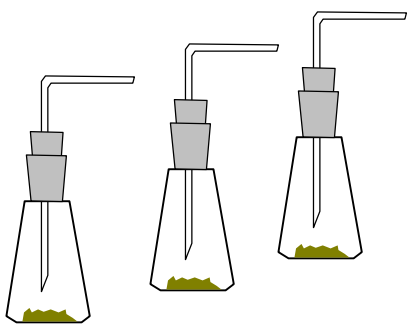
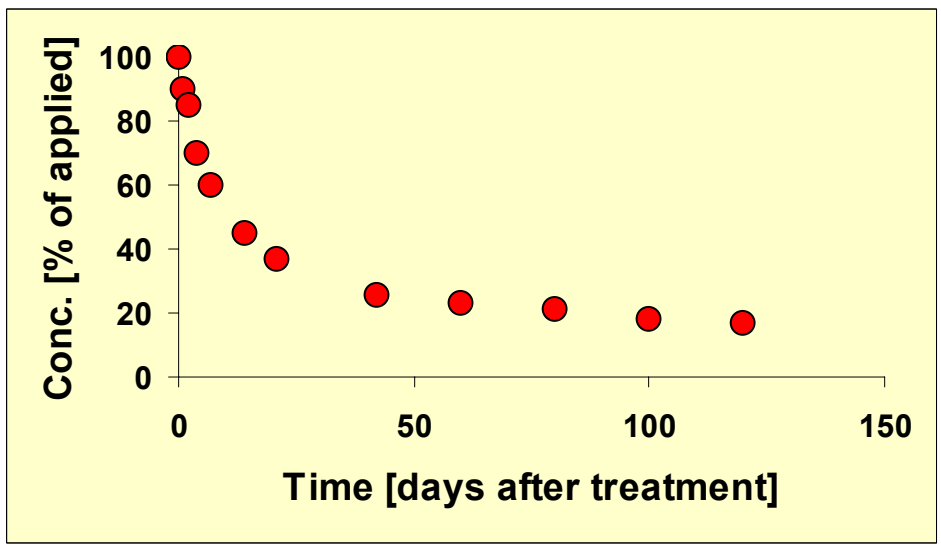
Example 2: Laboratory soil degradation study (Boesten, FOCUS kinetics report)

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**

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





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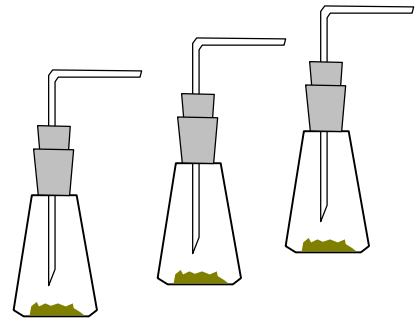
Example 2: Laboratory soil degradation study



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

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

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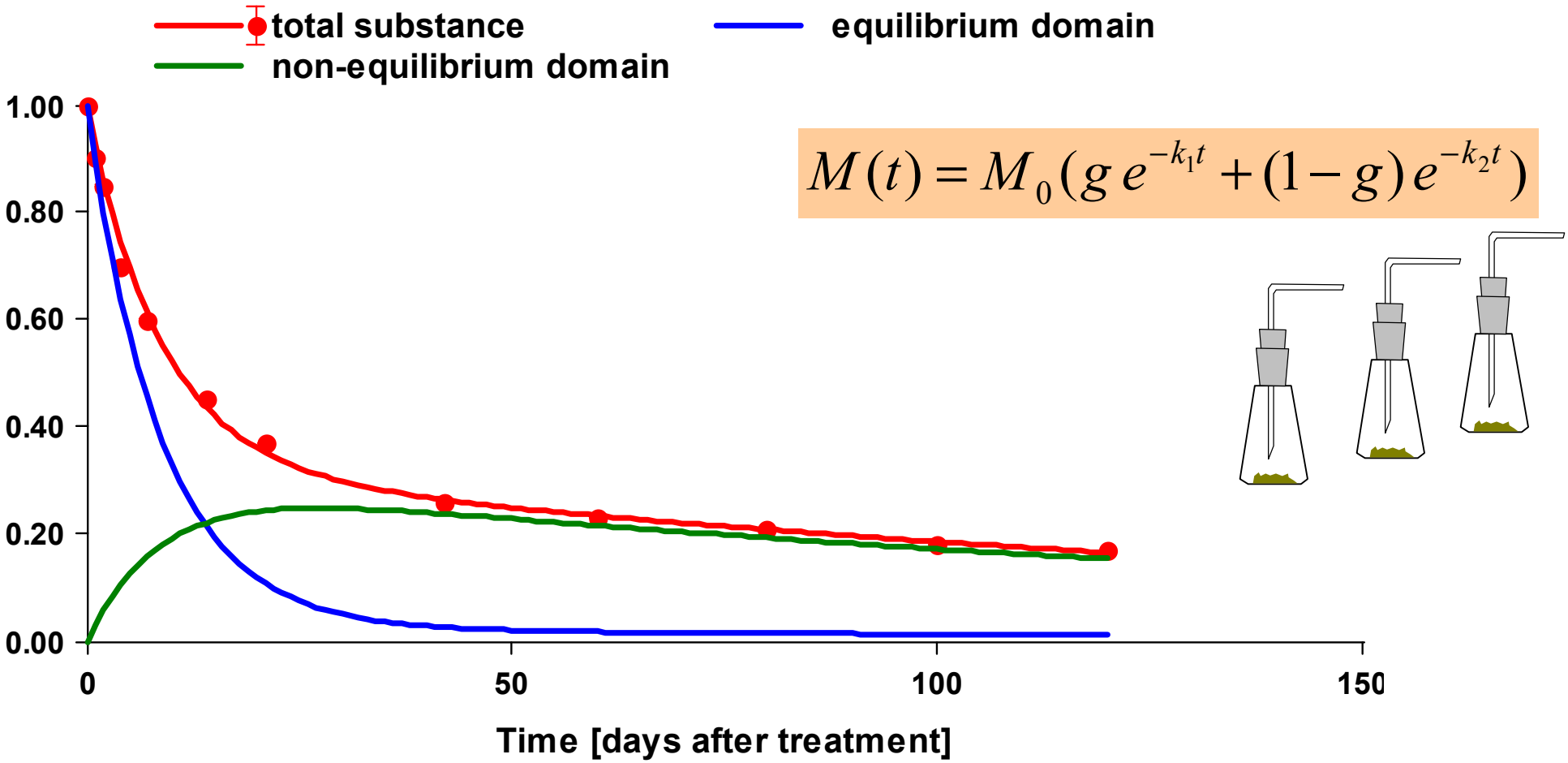
Higher tier evaluation of guideline studies

Example 2: Laboratory soil degradation study



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

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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 d^{-1}
  f_{NE} = *0.1 – 1*
- Correlation between parameters

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Higher tier evaluation of guideline studies

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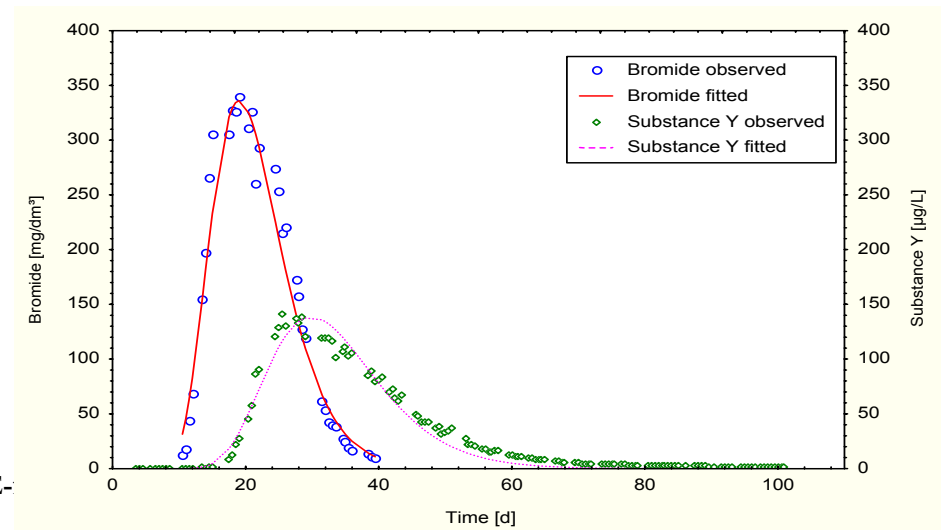
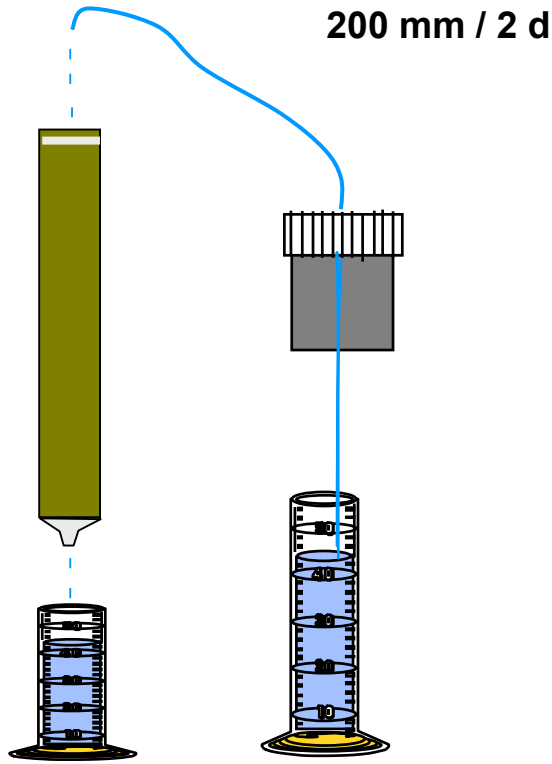
Example 3: Soil column (aged residues) studies

+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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Higher tier evaluation of guideline studies

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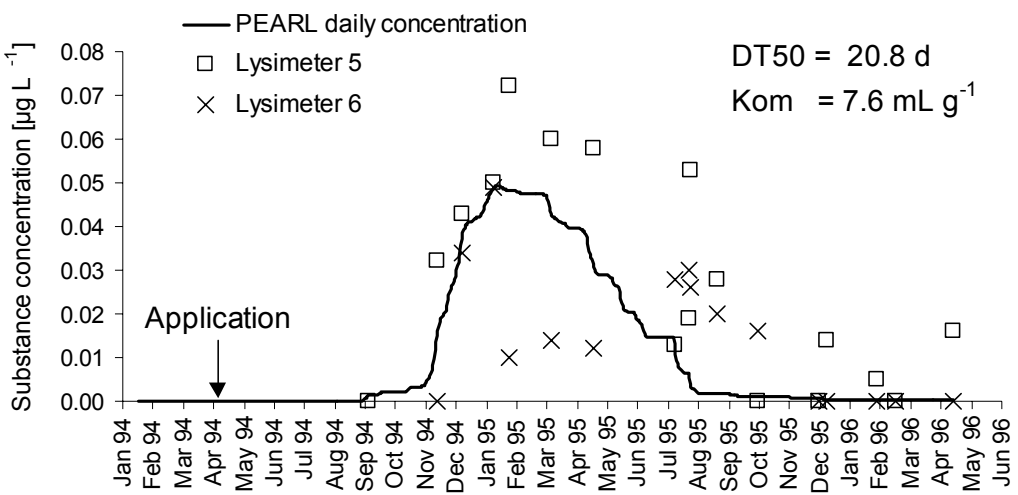
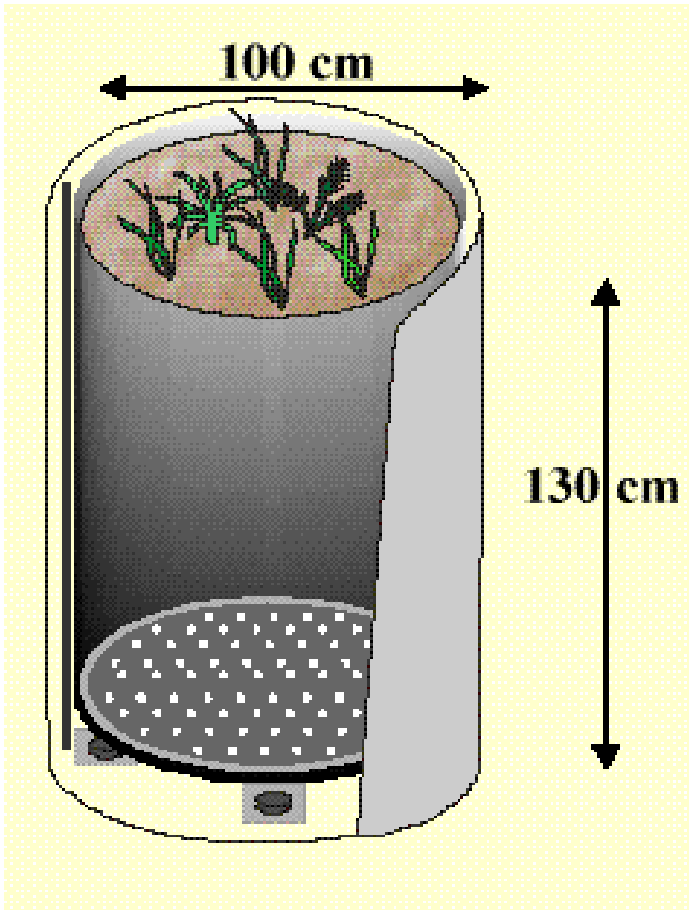
Example 4: Inverse modelling of outdoor lysimeter studies

- evaluation of water outflow (ETact)
- evaluation of BTC

- high number of influencing variables





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Higher tier evaluation of guideline studies

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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

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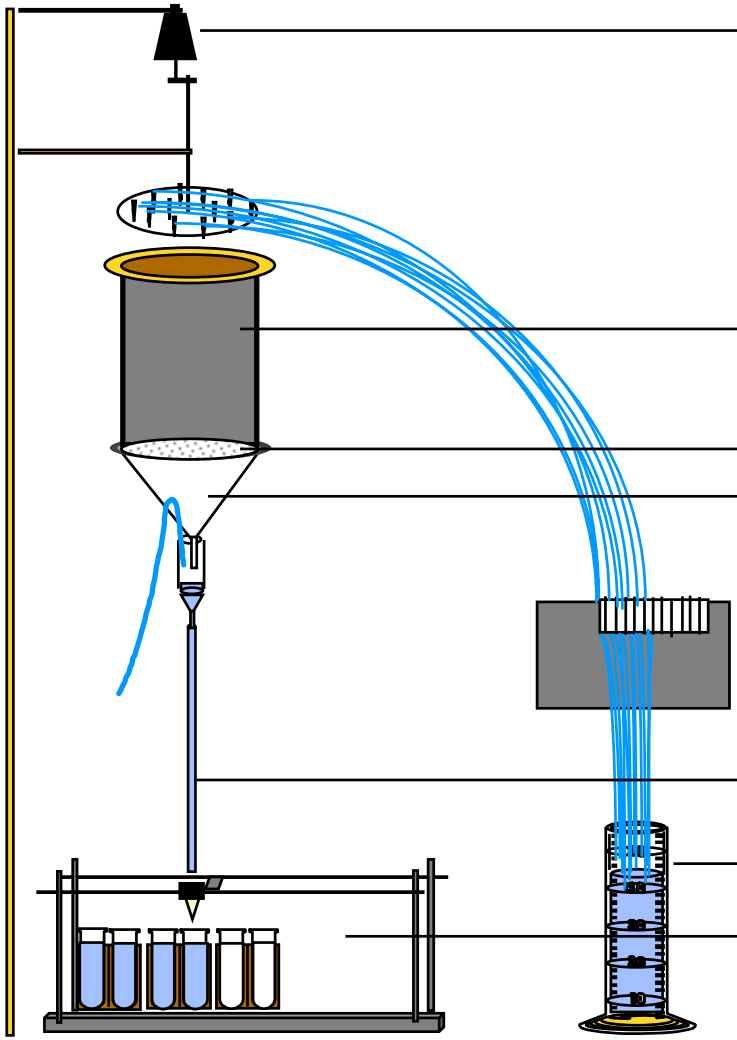

Motor of the irrigation device

Soil column, ∅ = 19,6 cm , h = 30 cm

porous ceramic plate

glass funnel

Tube with water column

Irrigation solution = 0,01M $CaCl_2$

Fraction sampler for percolate

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Higher tier studies: Microlysimeter

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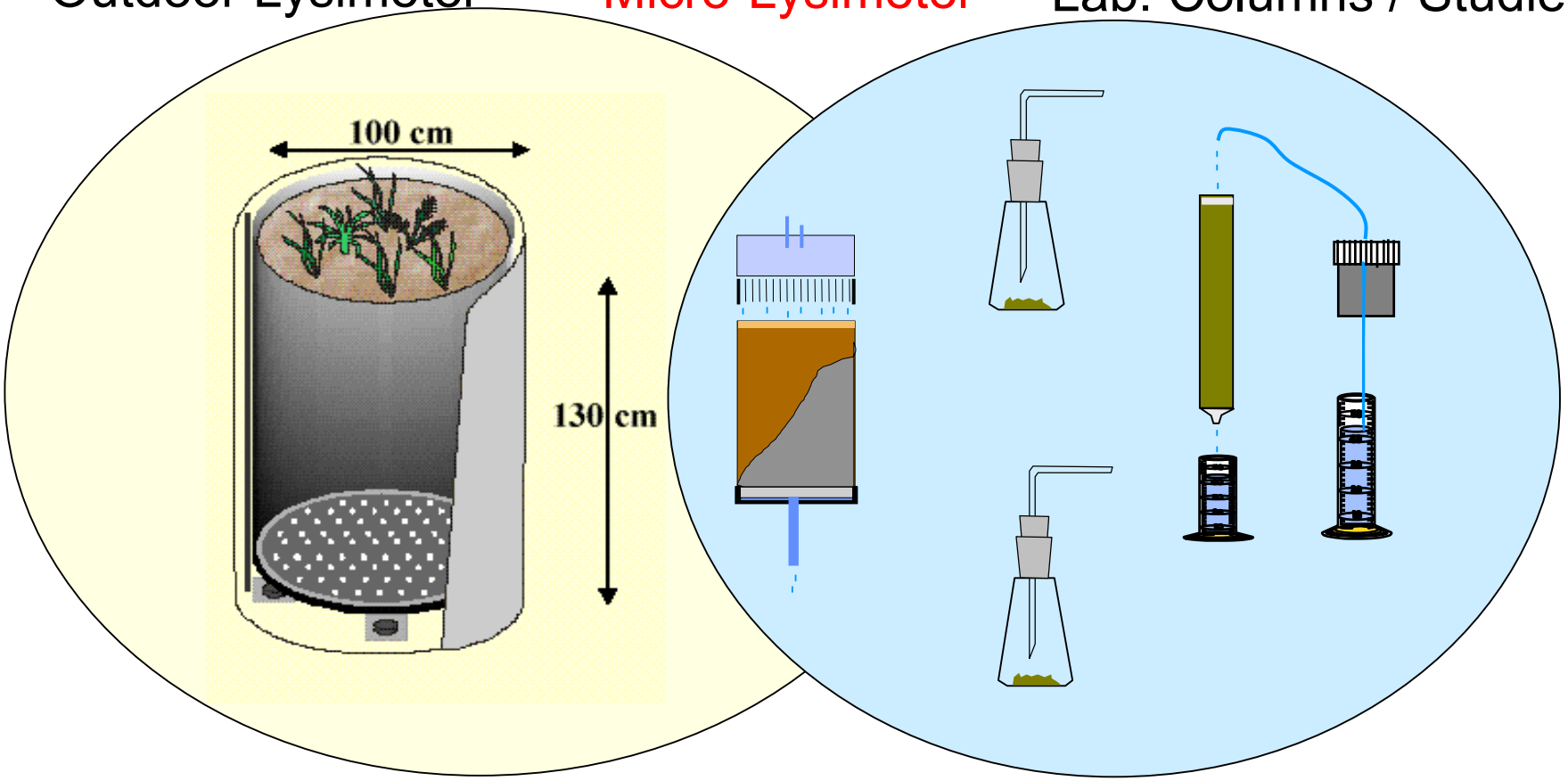
Outdoor Lysimeter Micro-Lysimeter Lab. Columns / Studies



- 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

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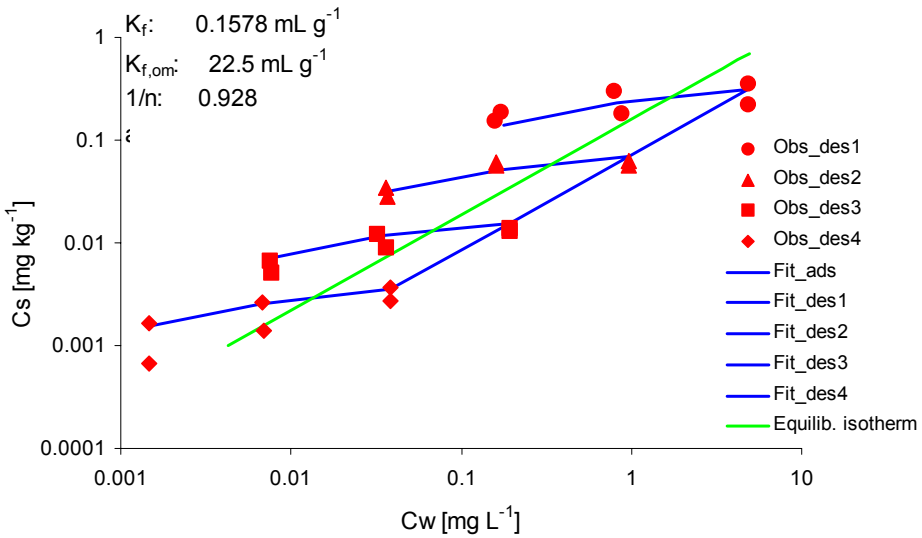
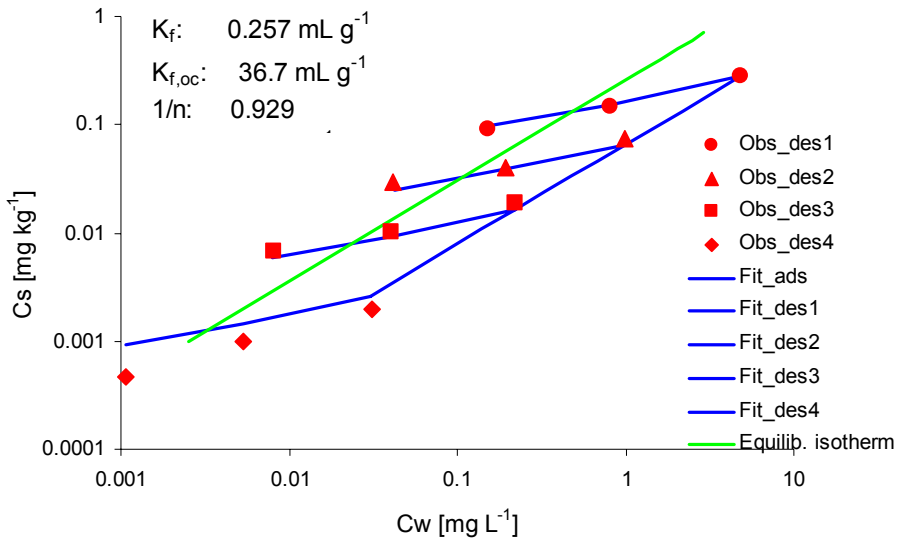
Case study: higher tier sorption

Part 1: evaluation of ads-des OECD 106 studies





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Case study: higher tier sorption

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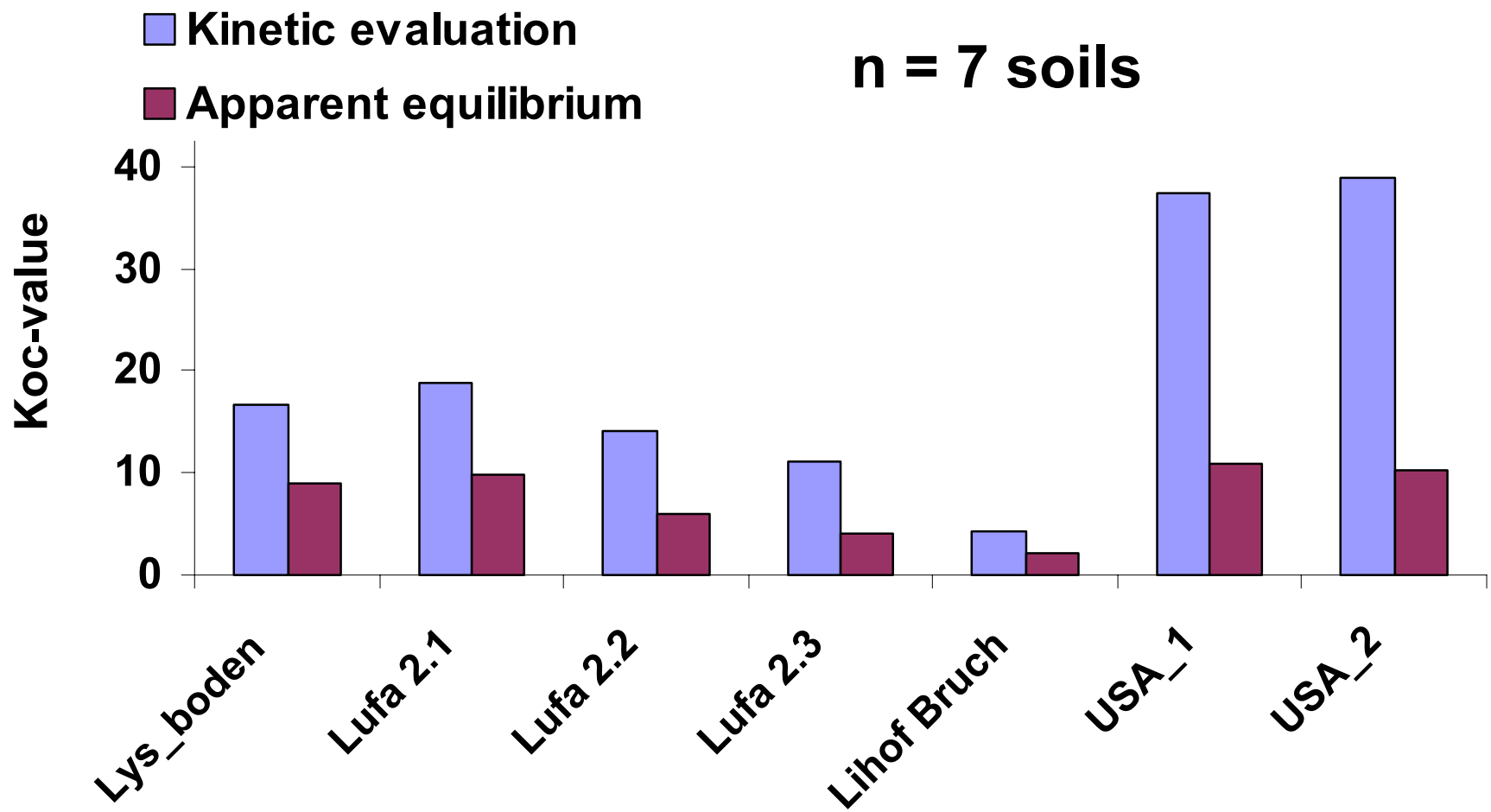
Part 1: evaluation of ads-des OECD 106 studies



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Case study: higher tier sorption

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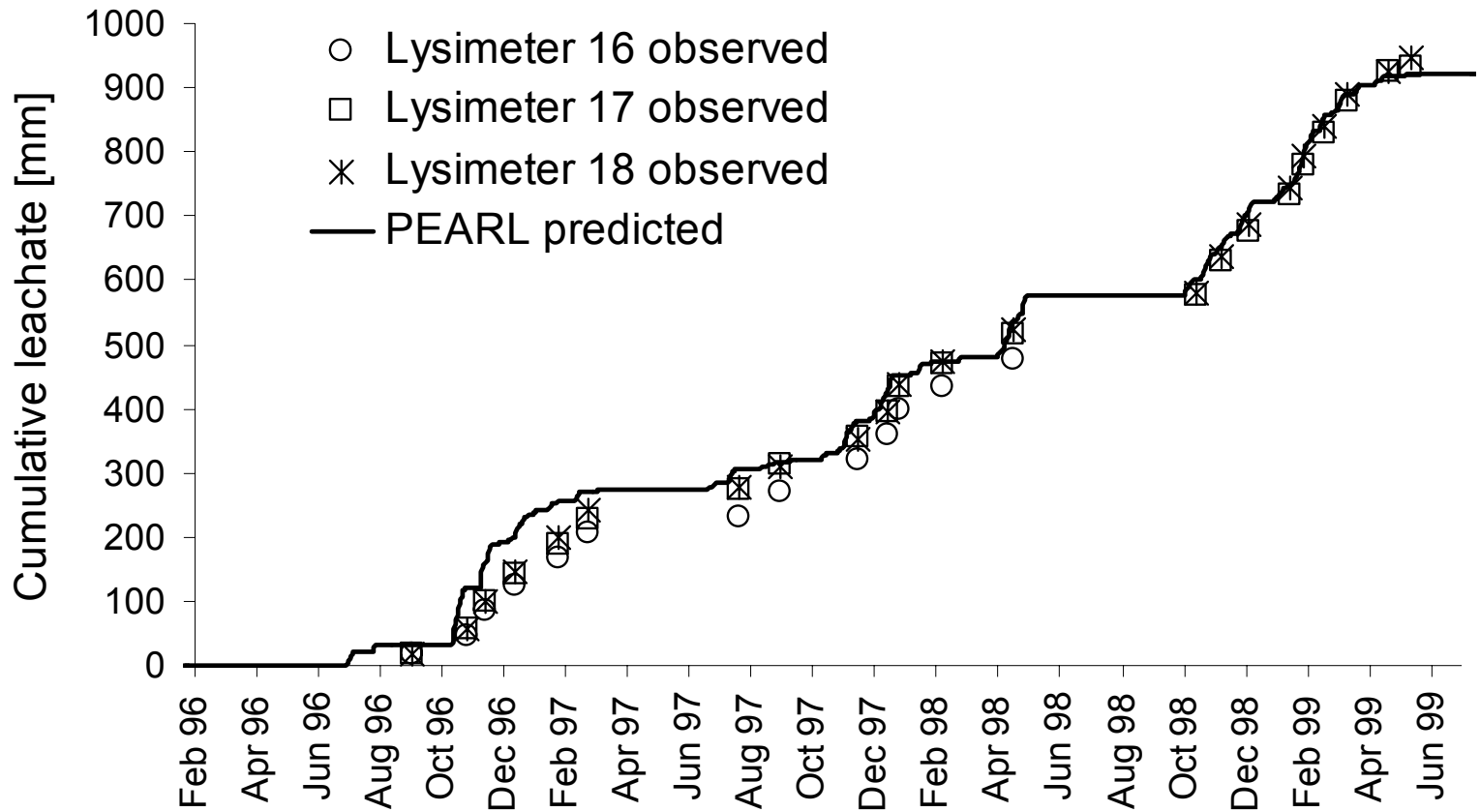
Part 2: inverse modelling of lysimeter studies (n = 5 lysimeter)



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Case study: higher tier sorption

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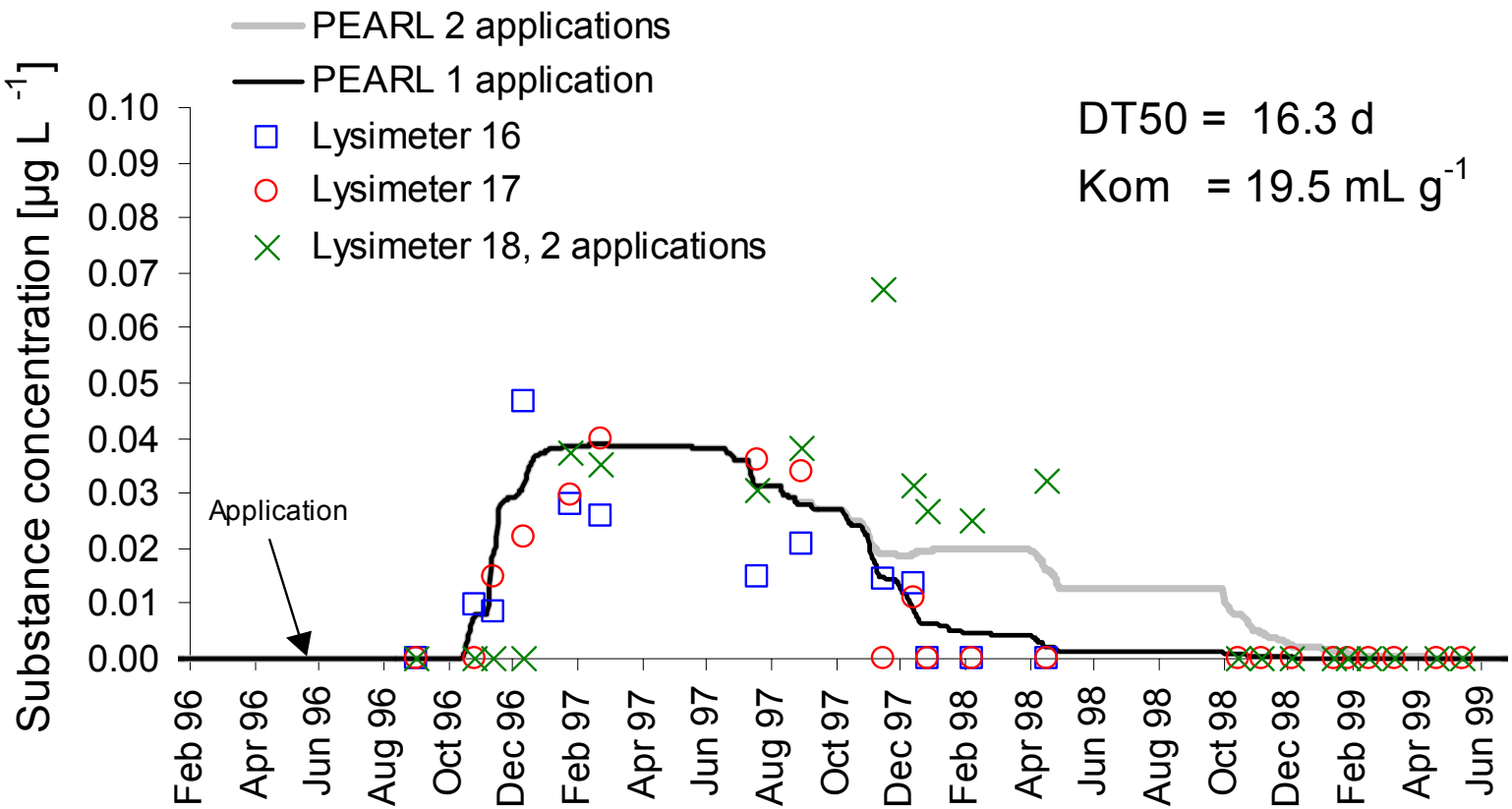
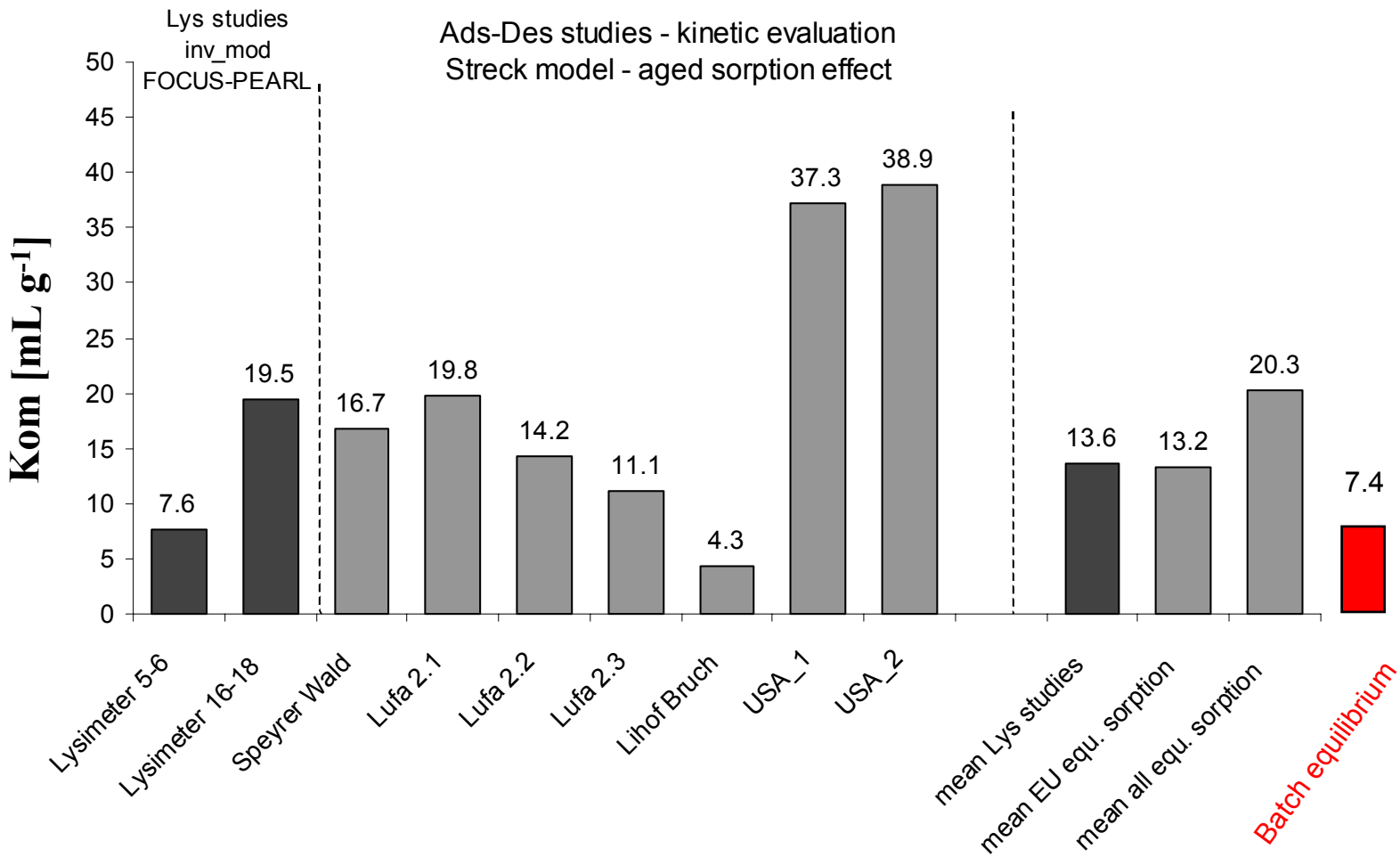
Part 2: inverse modelling of lysimeter studies



Case study: higher tier sorption



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Case study: higher tier sorption

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

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

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Case study: higher tier sorption

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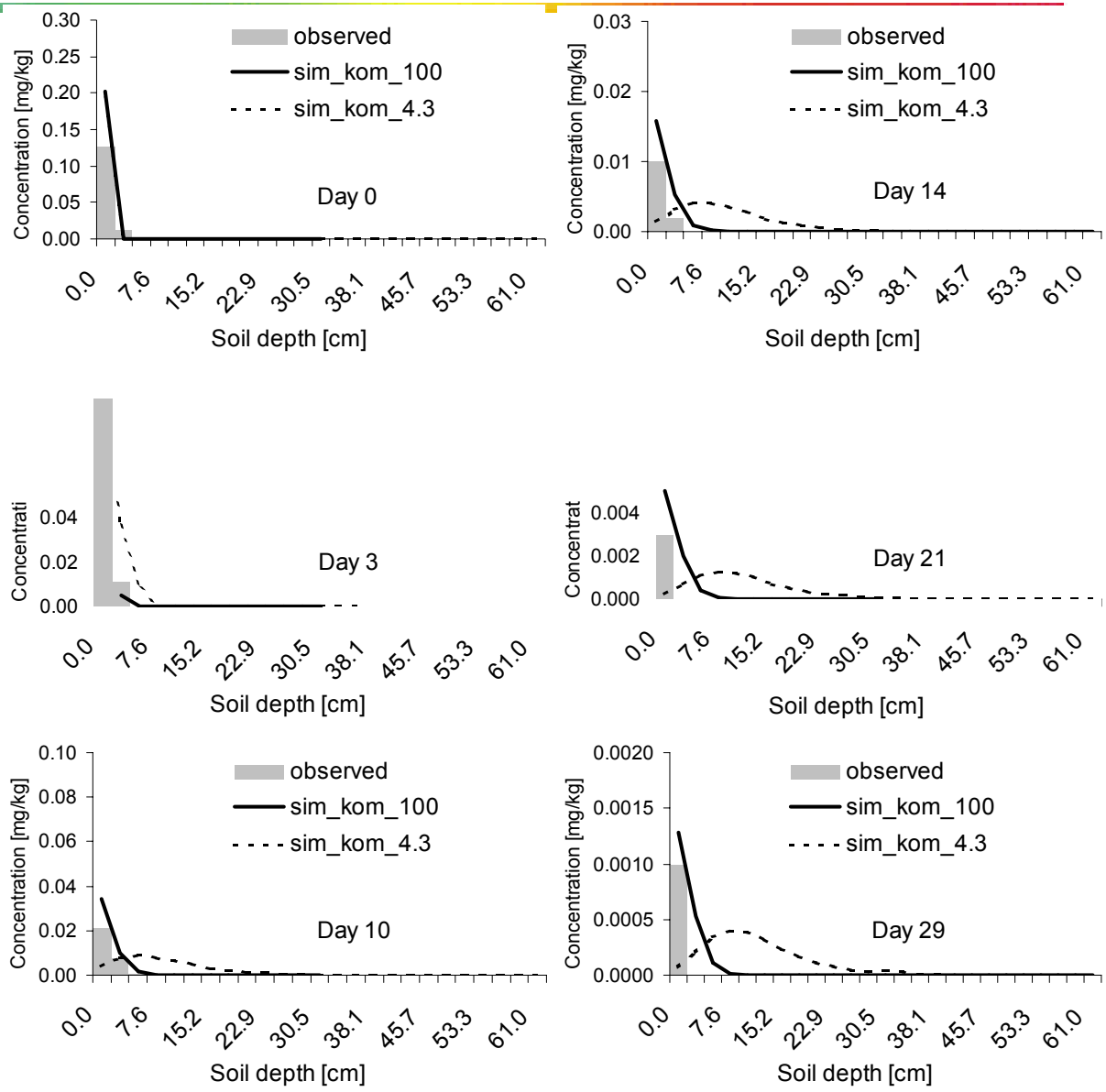
Part 3: evaluation of field studies (10 sites)



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Case study: higher tier sorption

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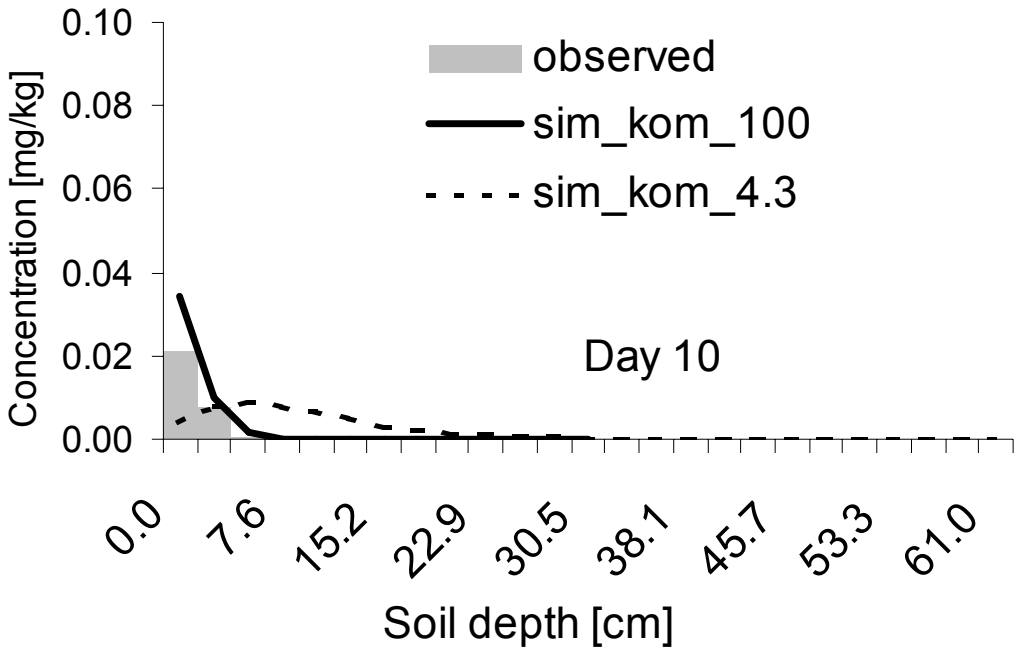
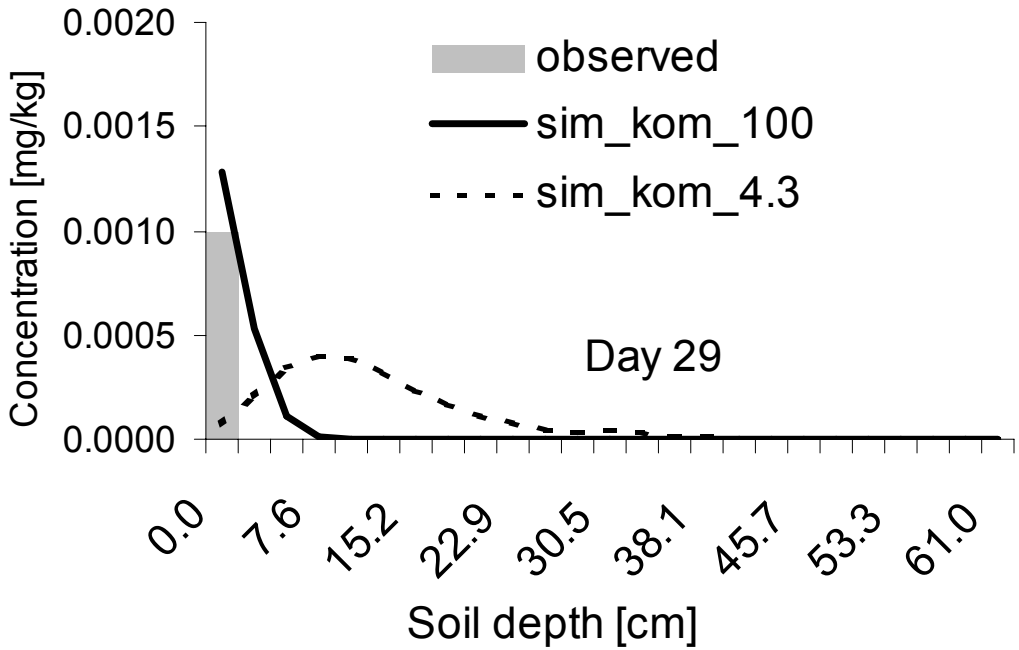
Part 3: evaluation of field studies (10 sites)
PEARL 1.1.1





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Case study: higher tier sorption

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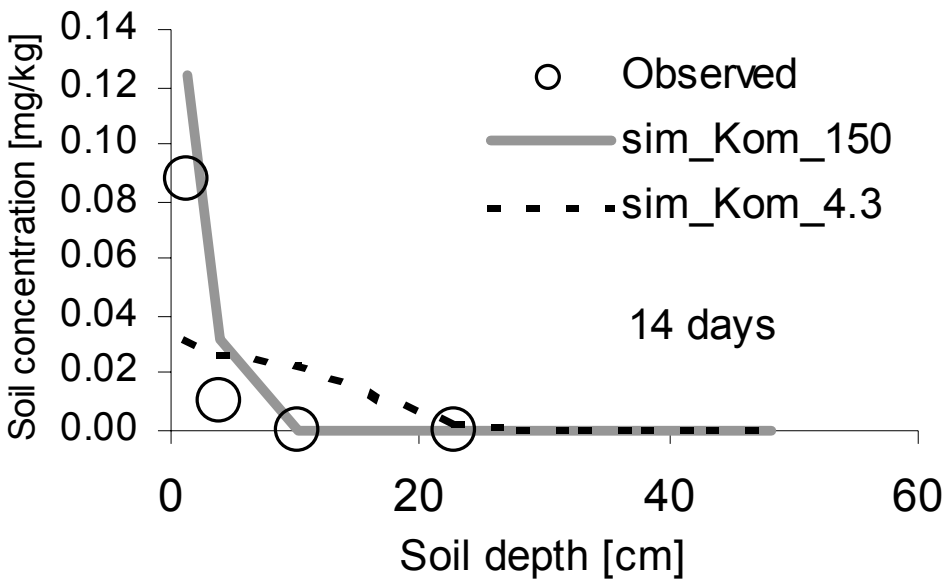
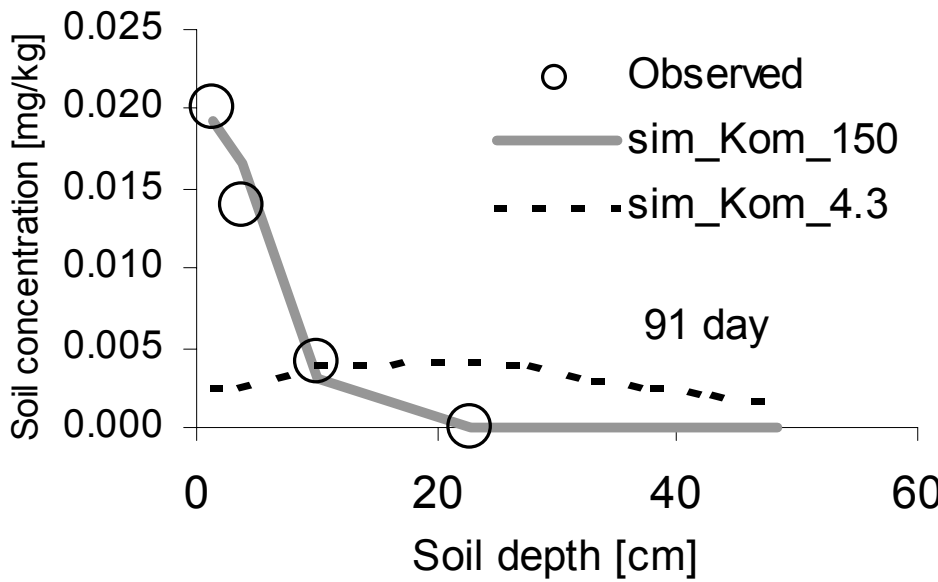
Part 3: evaluation of field studies (10 sites)
PEARL 1.1.1





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Case study: higher tier sorption

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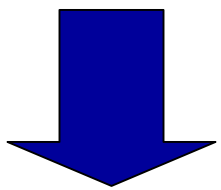
Part 3: evaluation of field studies (results)

- An agreement between simulated and observed concentrations could be achieved by using increased sorption values
- Using the apparent equilibrium Kom 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 Kom of the ads-des batch-equilibrium experiments

Overall conclusions

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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