Estimating non-equilibrium sorption parameters from concentration depth profiles of microlysimeter studies

Bernhard Jene

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Introduction

- **Process of non-equilibrium sorption**
  - **Theoretical and experimental evidence**
  - **Relevance is shown in scientific literature**
  - **Implemented in new guidance of FOCUS groundwater higher tier**
  - **Can be used in new versions of all FOCUS leaching models:**
    - **FOCUS-PEARL 4.4.4**
    - **FOCUS-PELMO 4.4.3**
    - **FOCUS-PRZM x.x.x**
    - **(FOCUS)-MACRO 5.1**
- **But how to derive non-equilibrium sorption parameters?**

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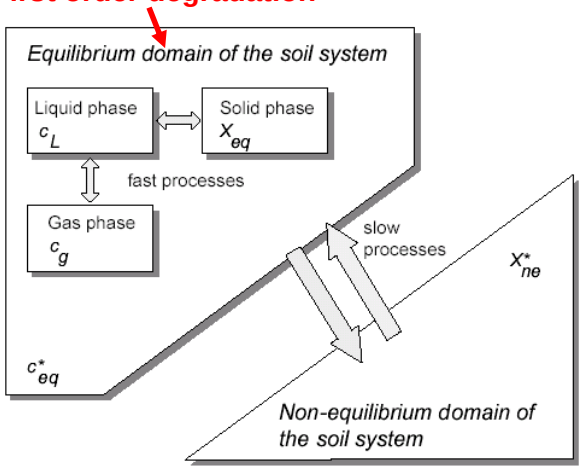
Theory

Non-equilibrium sorption in PEARL

- **Parameters needed:**
  - f_{NE} = ratio of NEQ-sorption and equilibrium sorption (e.g. $K_{f,om\text{-}neq}/K_{f,om\text{-}equ}$)
  - $K_{f,om\text{-}equ}$: Equilibrium sorption parameter (can be taken from batch study – OECD 106)
  - $DegT_{50\text{-}equ}$: Half-life in equilibrium phase
  - k_d = rate parameter controlling the transfer between equilibrium and NEQ phase

First order degradation



Recommendation from Pearl manual:

$f_{NE} = 0.5$

$k_d = 0.01\ d^{-1}$

No degradation

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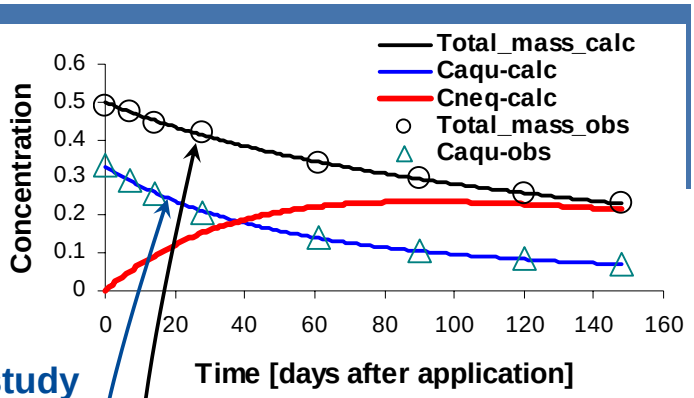
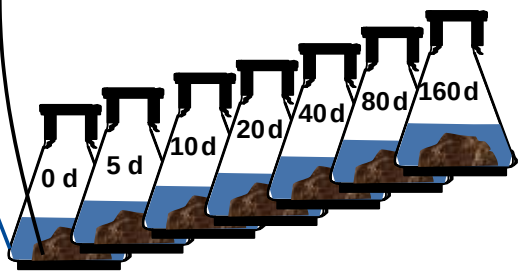
Standard approach



- **Aged-sorption study**
  - **Incubation of moist soil**
  - **Similar to lab degradation study (OECD 307)**
    - **Controlled conditions**
    - **Pre-treatment of soil (sieving)**
    - **Static system**
  - **Desorption with aqueous ($CaCl_2$) solution in addition to desorption with organic solvents**



⇒ **Often tested**

⇒ **Evaluation software available (Pearl_NEQ, Modelmaker)**

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Alternative approaches?

Hypothesis: ***Non-equilibrium sorption is a process that influences the transport behaviour of a chemical through (undisturbed) soil***

Approach: ***It should be tested whether it is possible to derive parameters from standardised leaching experiments showing a high level of realism (closer to outdoor conditions than "aged-sorption studies")***

Advantage: Parameters are identified in a system where the essential process (chemical transport) is tested

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The test system

- **Microlysimeters:**
  - **Undisturbed soil**
  - **Controlled boundary conditions**
  - **Realistic irrigation leads to soil water movement similar to outdoor conditions**
  - **Realistic suction at lower boundary assures unsaturated flow conditions**
  - **Use ^{14}C-labelled substances allows for mass balance**
  - **Analysis of outflow (BTC) and residue profile possible**

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The chemical

- **Model substance:**
  - Medium sorption in batch experiments according to OECD 106 ($K_{f,om} \approx 150$ mL/g)
  - Relatively slow degradation in lab (DT50 > 200 days)
  - Significant faster degradation in field (>factor 2)

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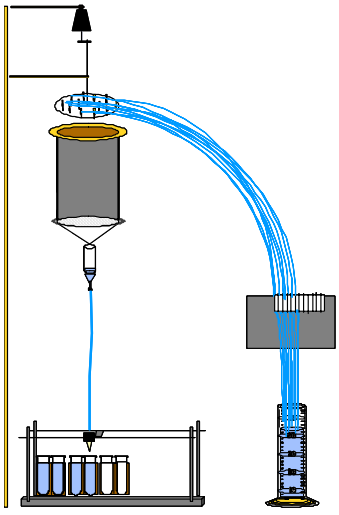
The experiment

- **3 soils**
  - loam with 6.5% OM
  - loamy sand with 4.3% OM
  - loamy sand with 1.0% OM
- **2 time intervals**
  - 120 days
  - 200 days
- **2 replicates**

12 individual columns



- **Application of bromide and test substance**
- **Irrigation cycle:**
  - 5 days of 3 mm per day
  - 2 days flow interruption
- **Lower boundary condition: constant potential of 50 hPa with hanging water column**

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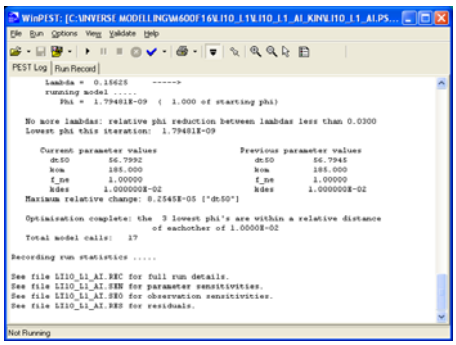
Parameter fitting strategy

Step 1: Fitting hydraulic parameters (using PEST and SWAP as in FOCUS-PEARL)

- Correction of infiltration amount by average evapotranspiration ET_{act} (<10%)
- Initial guess of hydraulic parameters using PTF of HYPRES
- Using inverse modelling by fitting bromide BTC
- Fitting parameter set for each individual column
- Free parameters:
  - K_{sat}
  - θ_{sat}
  - dispersivity
  - Initial mass of bromide applied
- Check if bromide BTC is well fitted
- Check if outflow dynamics with flow interruption is sufficiently fitted (-> test if improvement is possible by fitting other hydraulic parameters such as α, λ, n)



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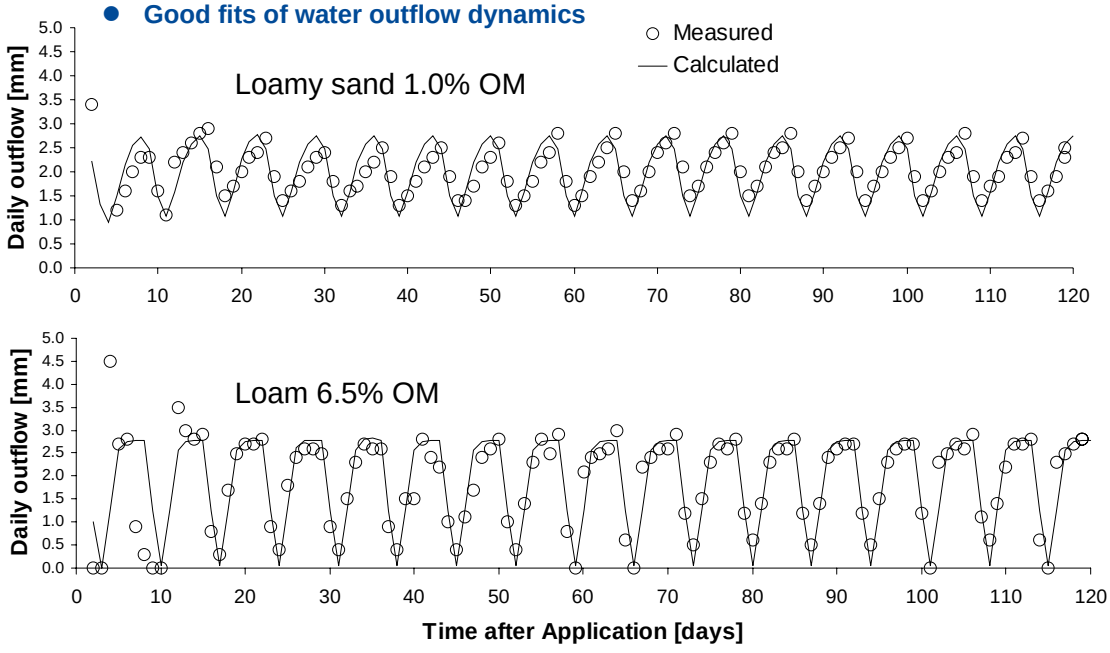
Hydraulic parameters

Step 1: Fitting hydraulic parameters

- Good fits of water outflow dynamics



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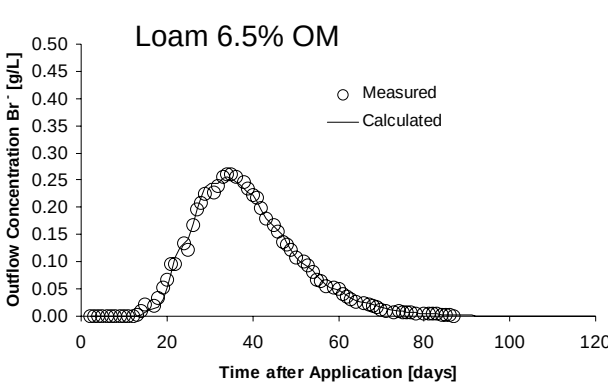
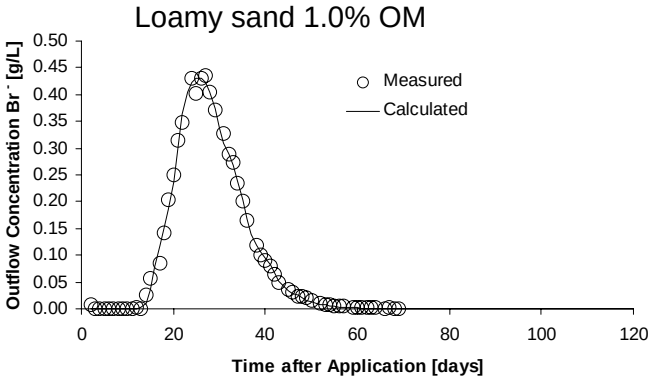
Results of hydrology fitting

Step 1: Fitting hydraulic parameters

- Excellent fit of bromide BTC -> all parameters significant





Fitted hydraulic parameters of the soil columns (standard deviation)

	θ [m^3/m^3]	K_{sat} [m day^{-1}]	Dispersivity [mm]
Loam 6.5% OM	0.27 (0.019)	0.30 (0.21)	13 (1.4)
Loamy sand 1% OM	0.28 (0.009)	0.36 (0.16)	11 (5.2)
Loamy sand 4.3% OM	0.33 (0.019)	0.95 (0.83)	10 (3.6)

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Substance transport parameters

Step 2: Fitting transport of reactive substance

- No substance found in the leachate -> only residue depth profile fitted
- Objective function:
  - Depth profile (concentration of single layers) -> *"sorption behaviour"*
  - Total remaining mass after the end of experiments -> *"degradation behaviour"*
- Different models tested:
  1. Only equilibrium sorption => $K_{f,om}$ fixed to batch value, $DegT_{50}$ fitted
  2. Only equilibrium sorption => $K_{f,om}$ and $DegT_{50}$ fitted
  3. NEQ sorption included =>($K_{f,om}$ fixed to batch value, f_{NE} and $DegT_{50\text{-}equ}$ fitted
- Overparameterisation of the model has to be avoided:
  - Freundlich exponent (1/n) fixed to mean of batch studies (≈ 0.9)
  - Desorption rate (k_d) of NEQ sorption fixed to default of 0.01 d^{-1}
- Different fitting techniques were tested
  - Fit of each single column
  - Fit of all columns of one soil

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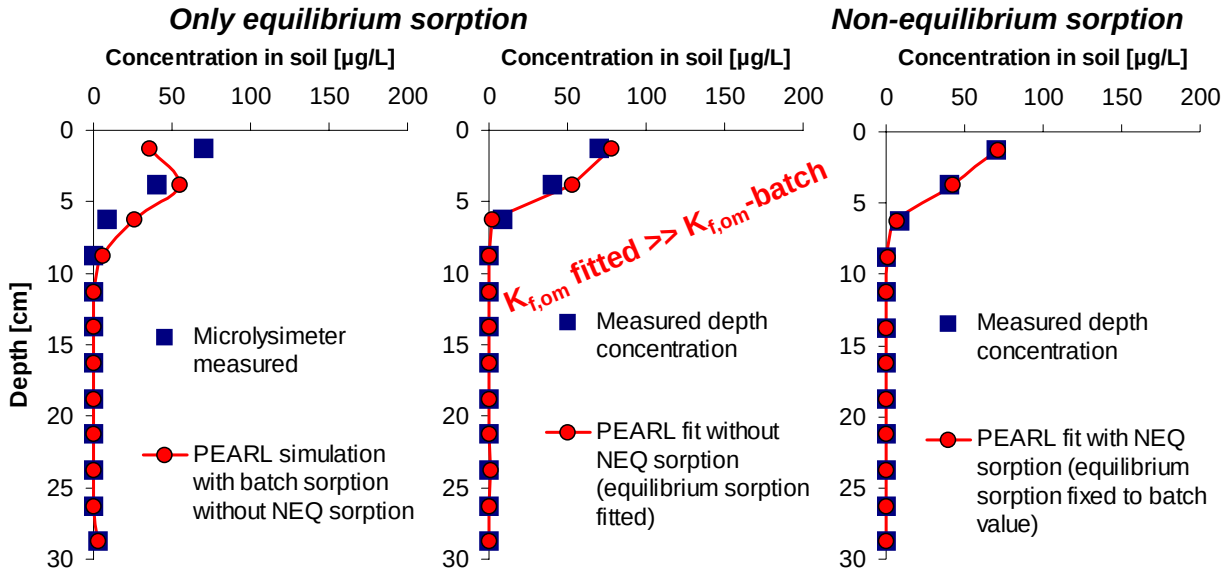
Results of substance transport

Step 2: Fitting transport of reactive substance -> Loamy sand 4.3% OM after 200 days



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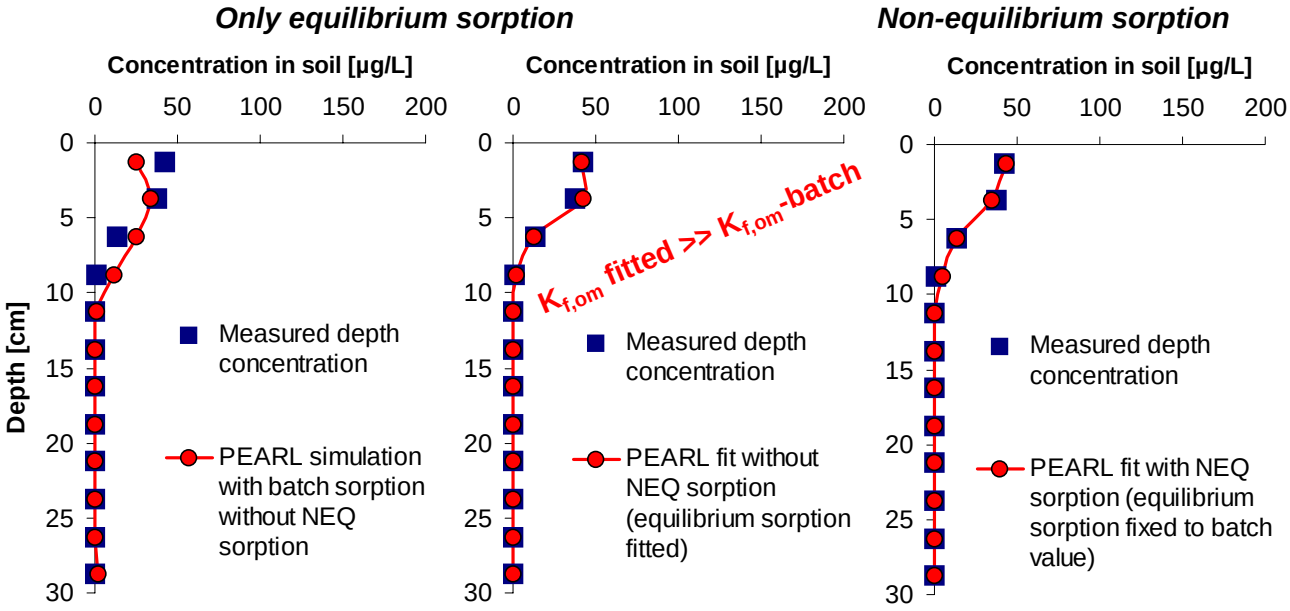
Results of substance transport

Step 2: Fitting transport of reactive substance -> Loam 6.5% OM after 200 days



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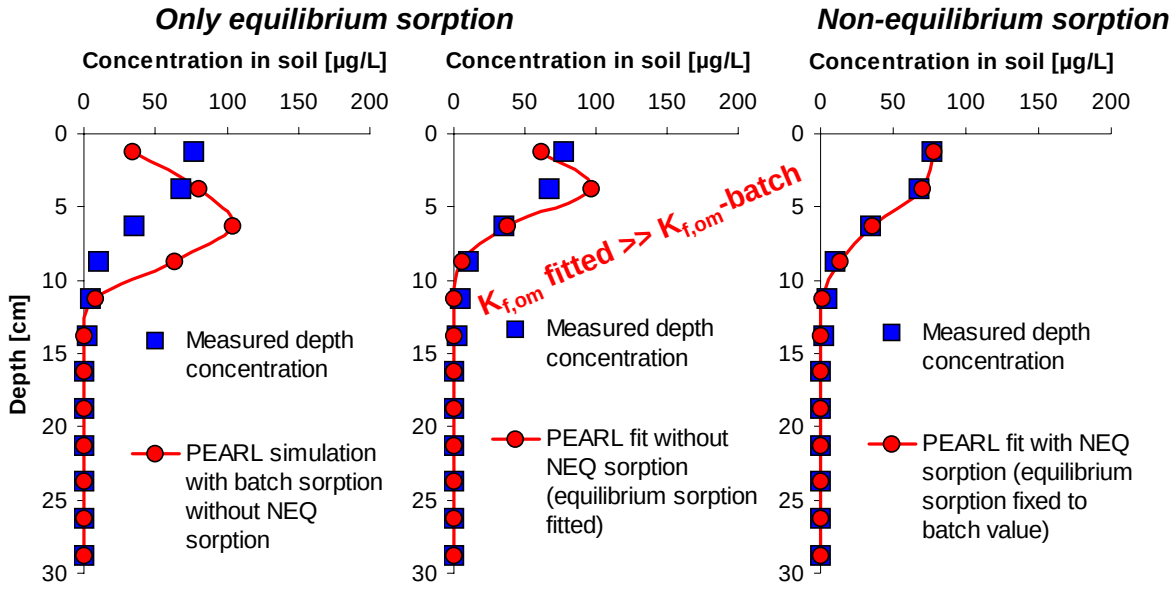
Results of substance transport

Step 2: Fitting transport of reactive substance -> Loamy sand 1% OM after 120 days



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Results of substance transport

First conclusions:

- **Equilibrium sorption with independent parameter (batch - $K_{f,om}$)**
  => overestimation of depth transport
  => shape of simulated depth profile differs significantly from measured

- **Equilibrium sorption with fitted sorption (estimated $K_{f,om}$)**
  => estimated $K_{f,om}$ from microlysimeter experiment much greater than batch-$K_{f,om}$
  => shape of simulated depth profile can differ significantly from measured

- **Non-equilibrium sorption transport with fitted NEQ-parameter (f_{NE})**
  => equilibrium sorption parameter from batch study can be used
  => shape of measured profile can be explained by model in all cases
  => rate parameter of NEQ sorption (k_d) has to be fixed to default (0.01 d^{-1})

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Results of substance transport

Step 2: Fitting transport of reactive substance with NEQ sorption

- **Excellent fit of depth concentration profiles (r^2 of all fits > 0.95)**
- **All estimated parameters significant at 5% error level**

Fitted non-equilibrium sorption parameters

	f_{NE}		$DegT_{50\text{-}equ}$	
	single fit	joint fit	single fit	joint fit
	[-]	[-]	[days]	[days]
Loam 6.5% OM	1.11	1.36	48.9	39.4
Loamy sand 1% OM	0.81	0.76	87.9	82.6
Loamy sand 4.3% OM	1.06	1.22	56.5	49.3
mean	1.01	1.11	61.6	57.1
CV	41%	28%	33%	23%

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Summary and Conclusions

- Microlysimeters were used to estimate NEQ sorption parameters from depth profile concentrations of a medium sorbing compound
- In comparison to ***aged sorption*** studies ***microlysimeters*** represent a study design with a higher degree of realism concerning outdoor conditions:
  - **Greater soil volume**
  - **Undisturbed soil** *versus* **pre-treated soil (drying and sieving)**
  - **Unsaturated water and solute transport** *versus* **static conditions**
  - **Realistic daily infiltration rates**
  - **Less extrapolation necessary from leaching experiment to PEC_{gw}**
- The system is sensitive to parameters f_{NE}, $DegT_{50\text{-}equ}$ but not to the de-sorption rate k_d (has to be adjusted to default)
- Care should be taken that the spatial resolution of the depth profile is high enough
- The results show that the microlysimeters are appropriate to derive significant NEQ sorption parameters (f_{NE}, $DegT_{50\text{-}equ}$) for medium sorbing substances

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Summary and Conclusions

Thank you for your attention

Questions ?

Bernhard Jene

bernhard.jene@basf.com