Bayer CropScience

Assessment of time-dependent sorption in laboratory aged sorption, undisturbed soil column and field studies

Klaus Hammel

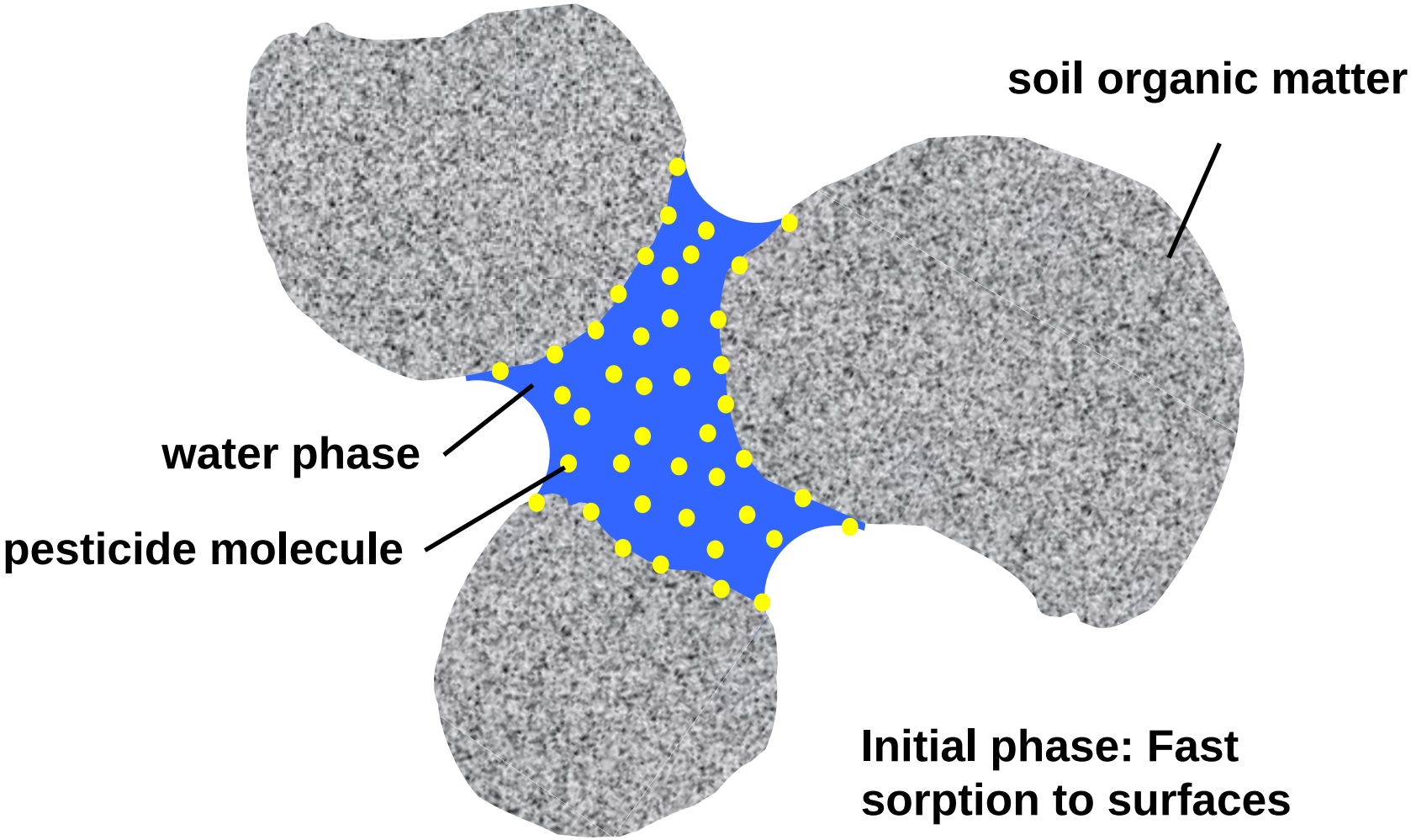
Conceptual Model of TDS

Different mechanisms leading to slow sorption

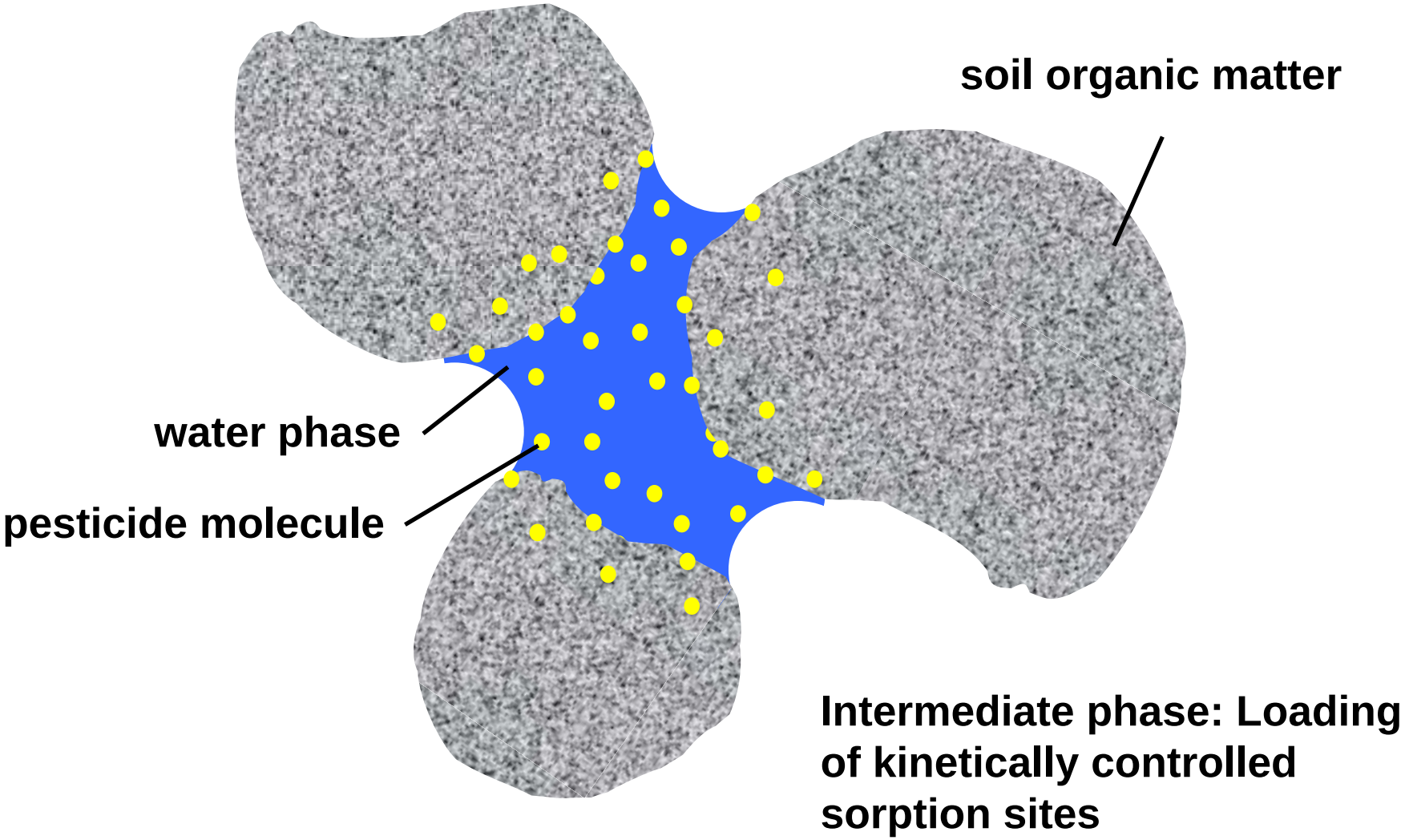
•retarded diffusion into intraparticular pore space accompanied by equilibrium sorption to the organic pore surface

•diffusion within soil organic matter

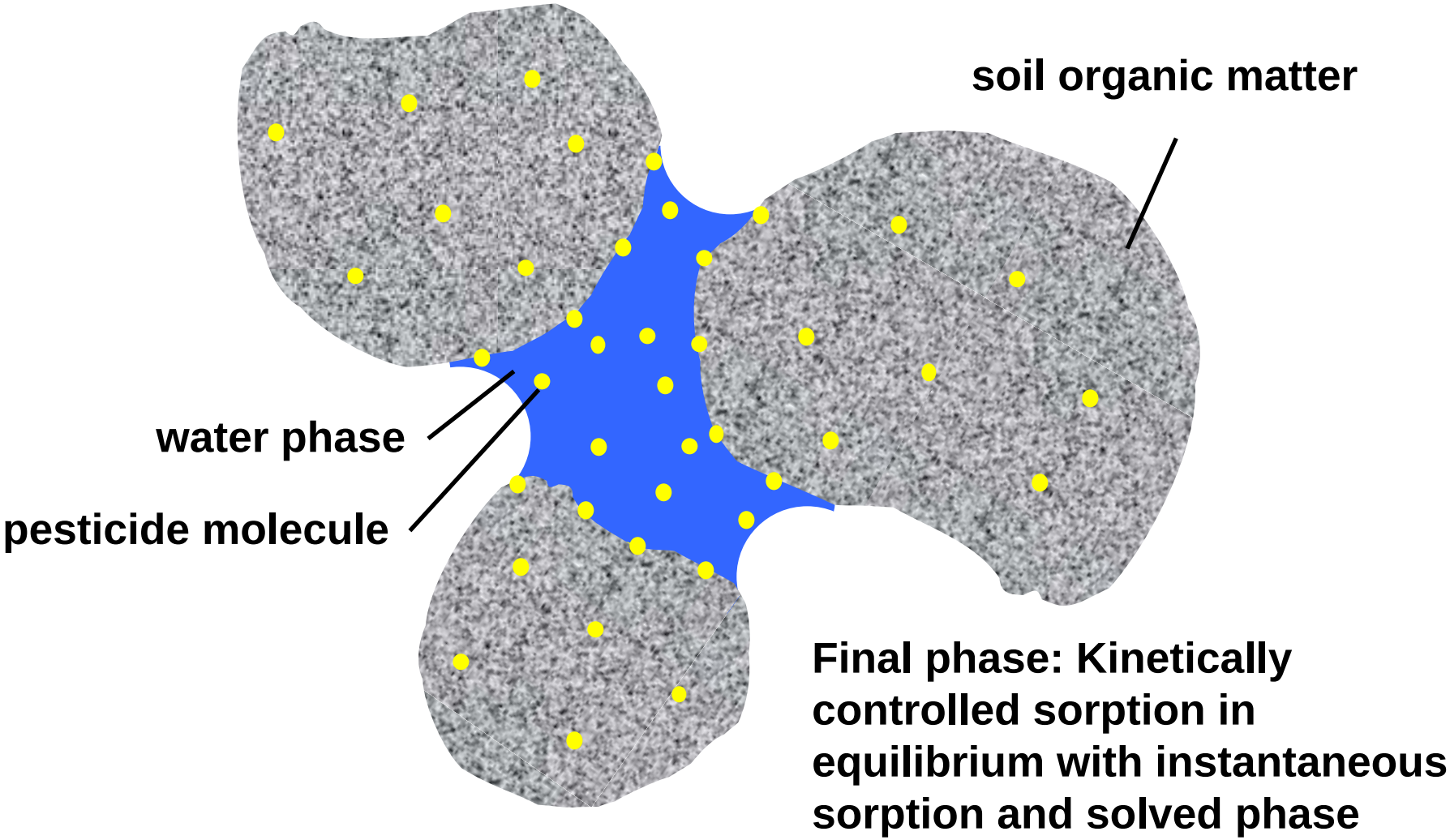
Conceptual Model of TDS



Conceptual Model of TDS



Conceptual Model of TDS

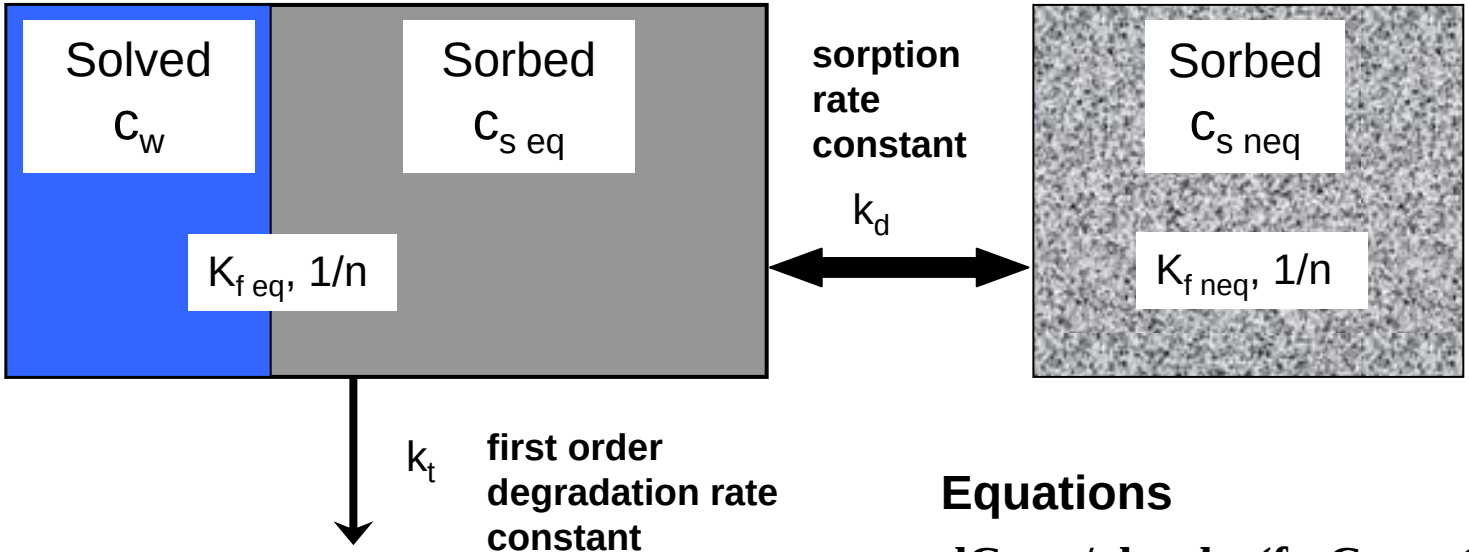


Mathematical Model of TDS

Kinetic sorption model recommended by FOCUS workgroup and implemented in PEARL (chemical transport model used in EU pesticide regulation)

Fast sorption ("equilibrium") domain

Kinetic sorption ("non-equilibrium") domain



Equations

$$dC_{s\ neq} / dt = k_d (f_{ne} C_{s\ eq} - C_{s\ neq})$$

$$f_{ne} = K_{f\ neq} / K_{f\ eq}$$

Impact of TDS on Leaching

- **Although the $DT50_{eq}$, i.e. $\ln(2)/k_t$ is typically lower than $DT50_{bulk}$ the overall degradation process is equivalently described**

- **TDS directly increases the retardation of a compound**

- **TDS leads to reduction of leaching by increasing the time for degradation before the target depth is reached**

Confirmation by Field Data

A number of field trials comfirm the relevance of kinetic sorption

Example 1: Succesful application of time dependent sorption parameters measured in the laboratory to the field (Boesten et al., Pestic. Sci., 1989)

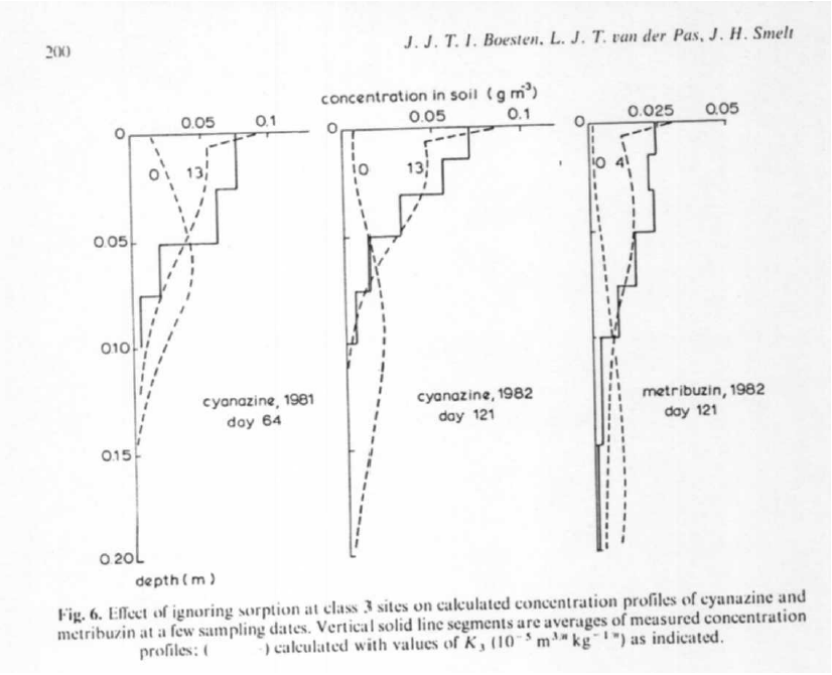
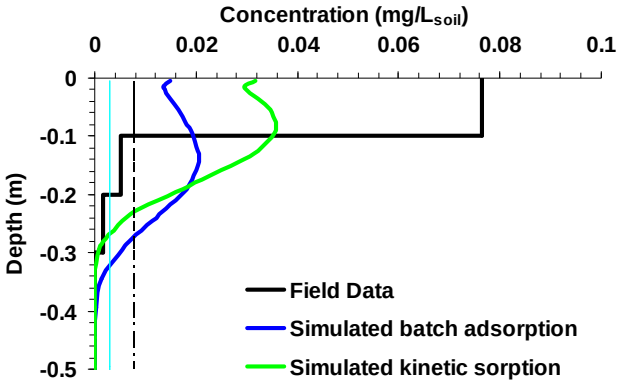


Fig. 6. Effect of ignoring sorption at class 3 sites on calculated concentration profiles of cyanazine and metribuzin at a few sampling dates. Vertical solid line segments are averages of measured concentration profiles; ( ) calculated with values of K_3 (10^{-5} m$^{3.n}$ kg$^{-1.n}$) as indicated.

Example 2: More realistic description of measured depth profiles - typical result for our field trials



RLP Agroscience & Bayer Cropscience Experiments

TDS experiments are usually conducted in the laboratory (incubation under static environmental conditions, e.g. FERA/Alterra draft guidance)

Can TDS parameters derived form laboratory experiments be used to describe the field?

Are TDS parameters derived from static laboratory experiments consistent with dynamic, i.e. transport experiments?

RLP Agroscience & Bayer Cropscience Experiments

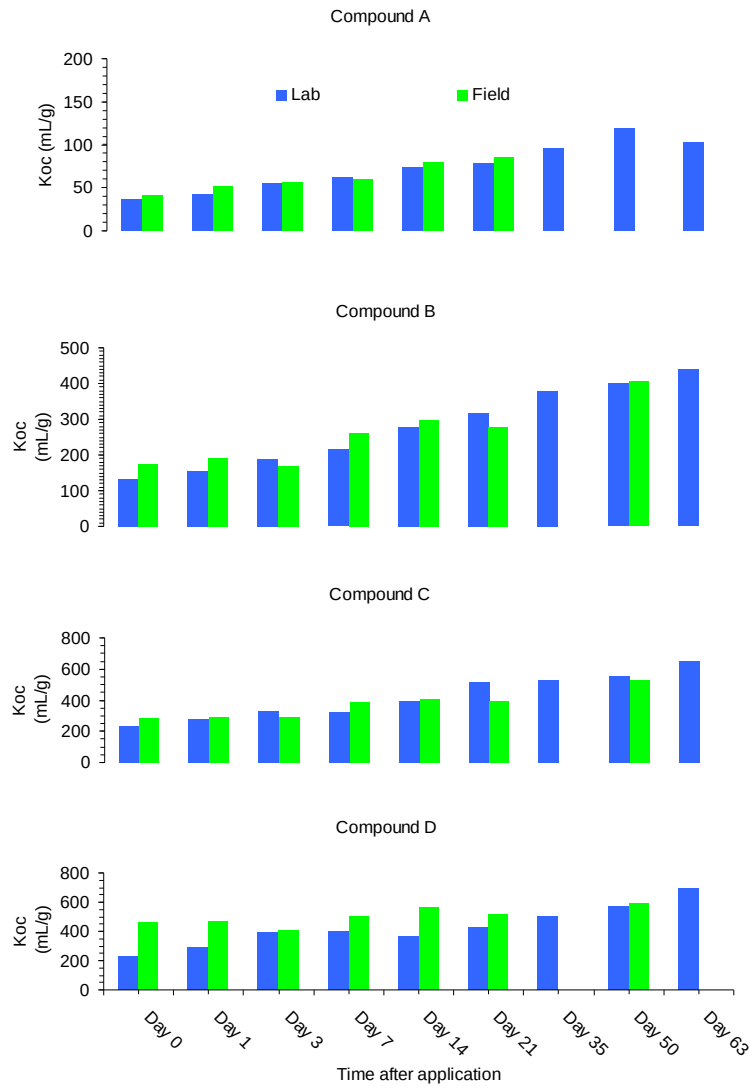
- **Time dependent sorption experiments with 4 compounds on the same 4 soils in the laboratory (incubation and column transport) and in the field**

Soil	Texture	OC (%)
AXXa	sandy loam	1.86
BH	sandy loam	0.79
HaH	silt loam	1.60
MB	sandy loam	0.80

Radio-labelled test substances with high to low water solubility was spiked to soil in the lab (as for OECD 307) and in the field (as overspray). Soil was extracted first with aqueous $CaCl_2$ solution for 24 hours, centrifuged, decanted and remaining soil exhaustively extracted with acetonitrile/water(3 times) and additionally under reflux conditions. Analysis by liquid szintillation counting and HPLC. Column experiments with undisturbed soil under steady state flow, evaluation of breakthrough and depth distribution.

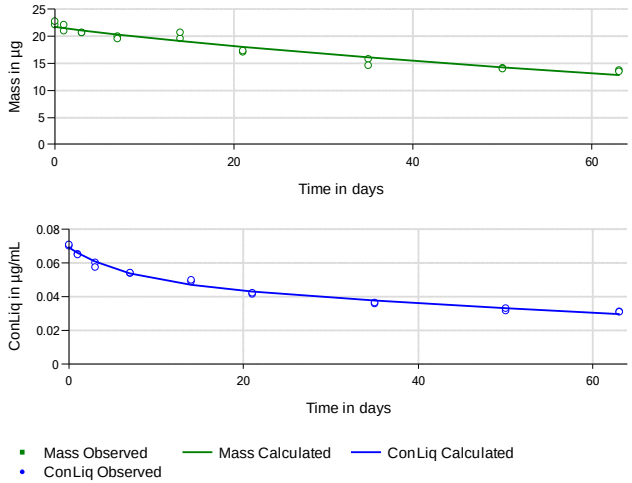
RLP Agroscience & Bayer Cropscience Experiments

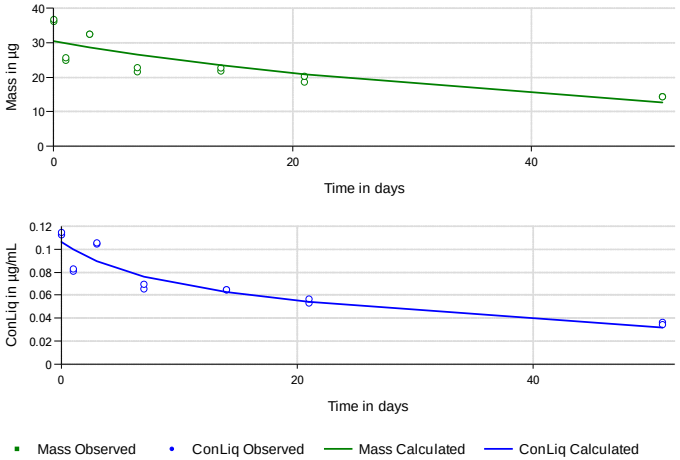
- **Increase of sorption with time measured in lab and field sample is essentially equivalent**



RLP Agroscience & Bayer Cropscience Experiments

Evaluation with kinetic sorption model (PEARLneq)





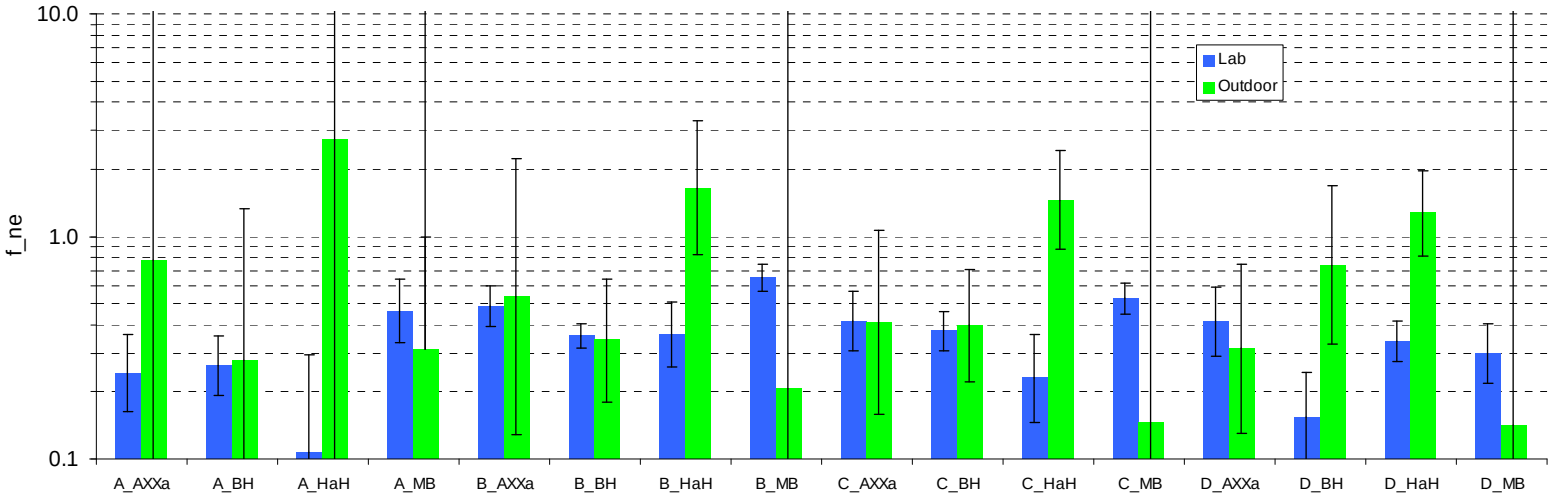
Satisfying results for lab incubation studies with regard to data scatter and parameter reliability

Increased data scatter and less reliable parameters for field samples

RLP Agroscience & Bayer Cropscience Experiments

Evaluation with kinetic sorption model (PEARLneq)

fitted to log transformed parameters, constant weights = 1/median of observation groups total mass and liquid concentration, error bars = +/- 1 std.dev



f_{ne} values from lab and field potentially equivalent, substantial uncertainty of the values derived from the field samples

RLP Agroscience & Bayer Cropscience Experiments

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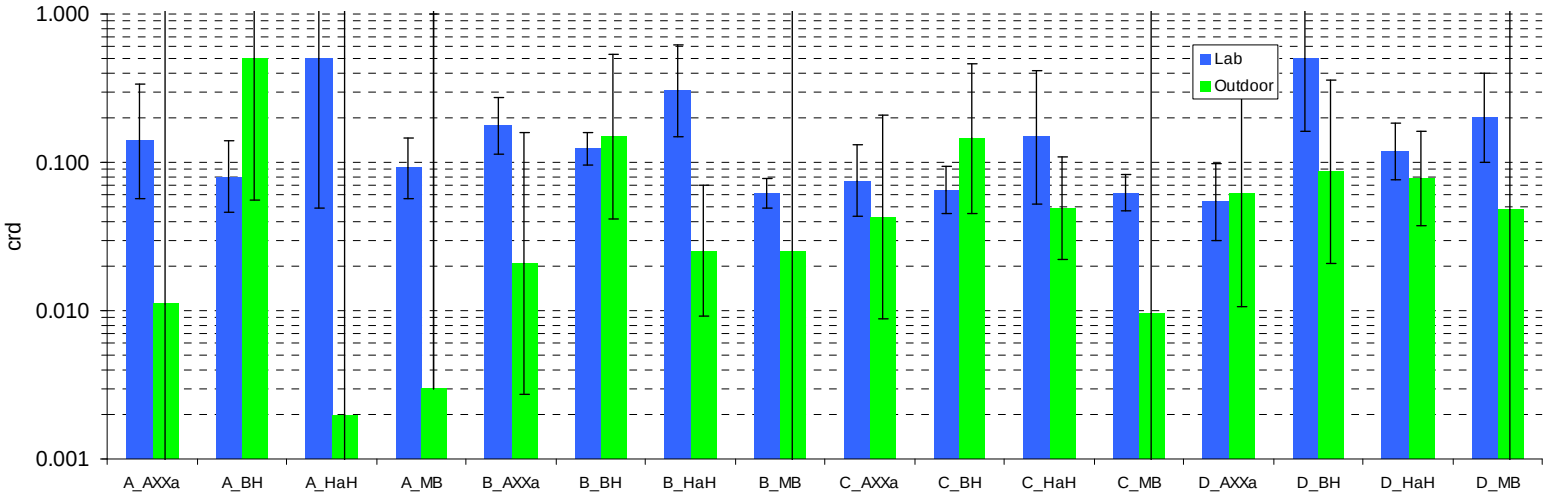
fitted to log transformed parameters, constant weights = 1/median of observation groups total mass and liquid concentration, error bars = +/- 1 std.dev

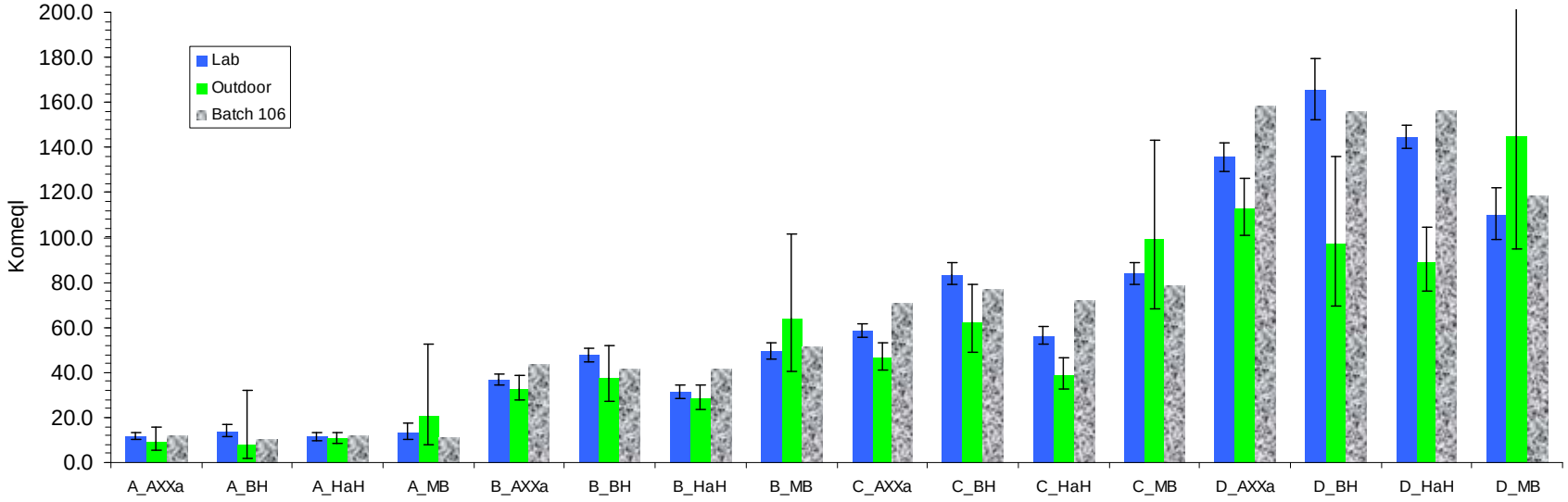


crd (k_D) values from lab and field potentially equivalent, substantial uncertainty of the values derived from the field samples

RLP Agroscience & Bayer Cropscience Experiments

Evaluation with kinetic sorption model (PEARLneq)

fitted to log transformed parameters, constant weights = 1/median of observation groups total mass and liquid concentration, error bars = +/- 1 std.dev



$K_{om\ eql}$ values from lab and field similar, in reasonable agreement with batch (OECD 106) K_{om}, higher uncertainty of values derived from the field samples

RLP Agroscience & Bayer Cropscience Experiments

Comparison TDS Laboratory – Field (Incubation experiments)

- **Apparent distribution coefficients and TDS parameter (incl. $K_{om\ eql}$) are similar for laboratory and field. No indication for systematic deviations.**

- **Large scatter in the field data does not allow strict statistical comparison**

- **Scatter is assumed to originate from inhomogeneous application. Improved study design is currently tested**

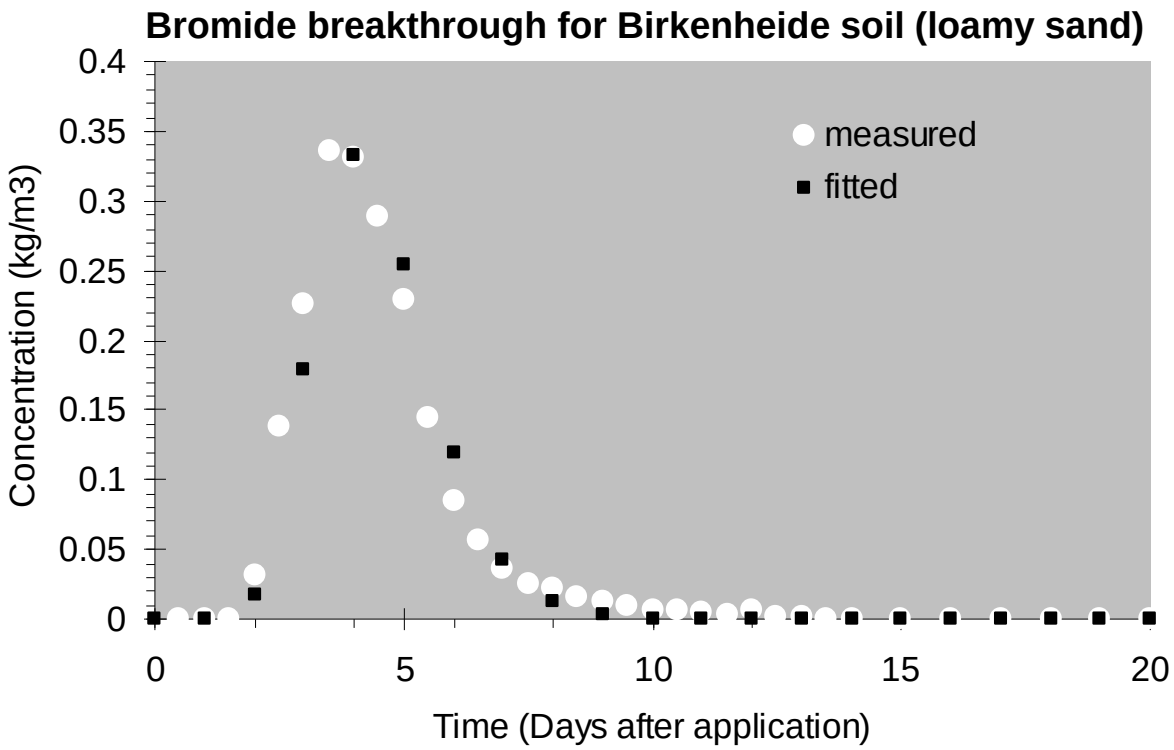
RLP Agroscience & Bayer Cropscience Experiments

First results of column experiments

- **Bromide tracer, compounds A, B, C, D applied as mixture**
- **Steady state flow, 15 mm/d (reduced to 7.5 mm/d in case of ponding) for about 90 days**
- **Undisturbed soil columns, 20 cm diameter, 20 cm long**
- **Constant head (- 30 cm) lower boundary condition**

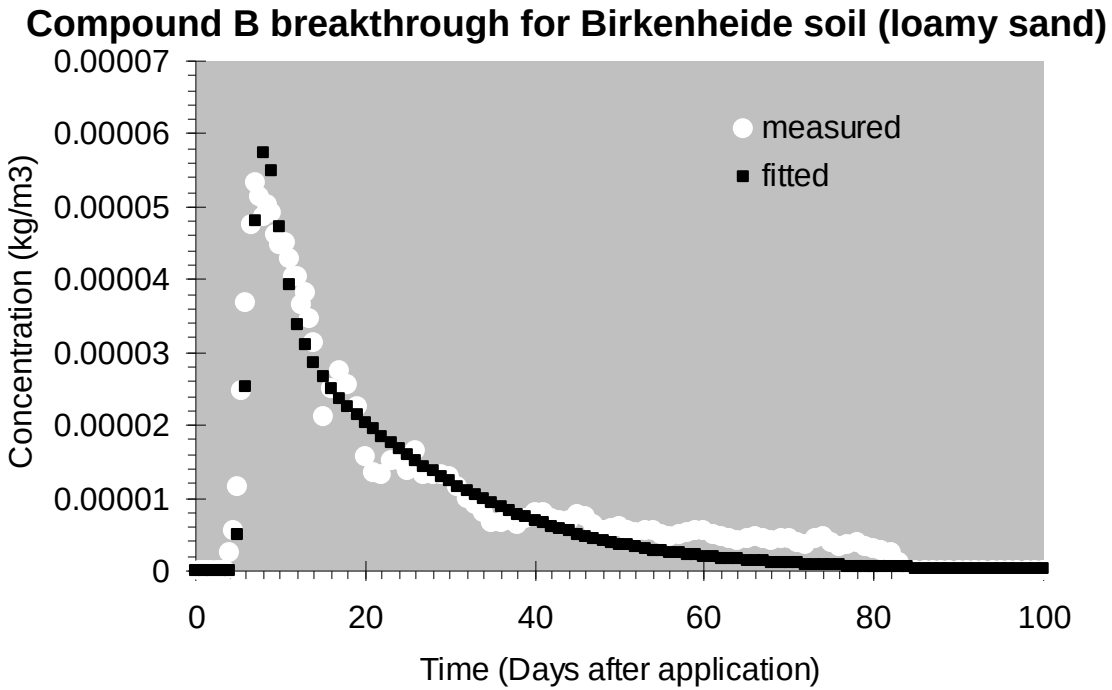
Undisturbed Soil Columns

Step 1: Fitting transport parameter to tracer data (water content and dispersion length)



Undisturbed Soil Columns

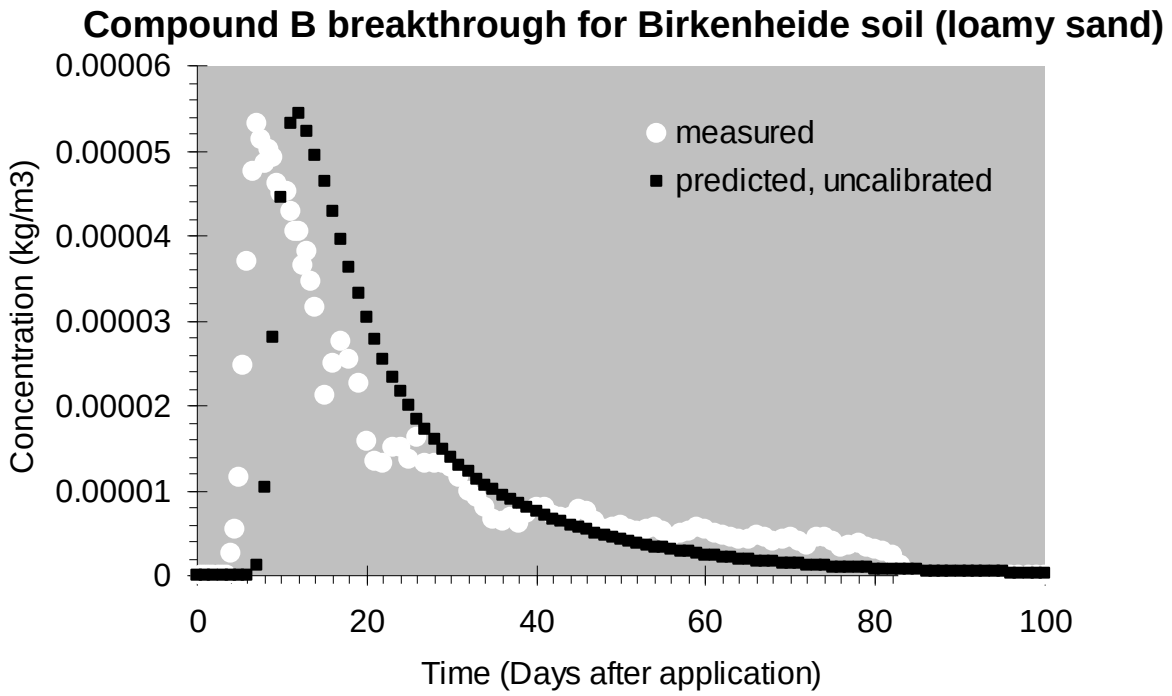
Step 2: Fitting kinetic sorption parameter to breakthrough curves (transport parameter fixed at Step 1)



First results indicate that breakthrough curves do not contain sufficient information to identify all kinetic sorption parameters (4)

Undisturbed Soil Columns

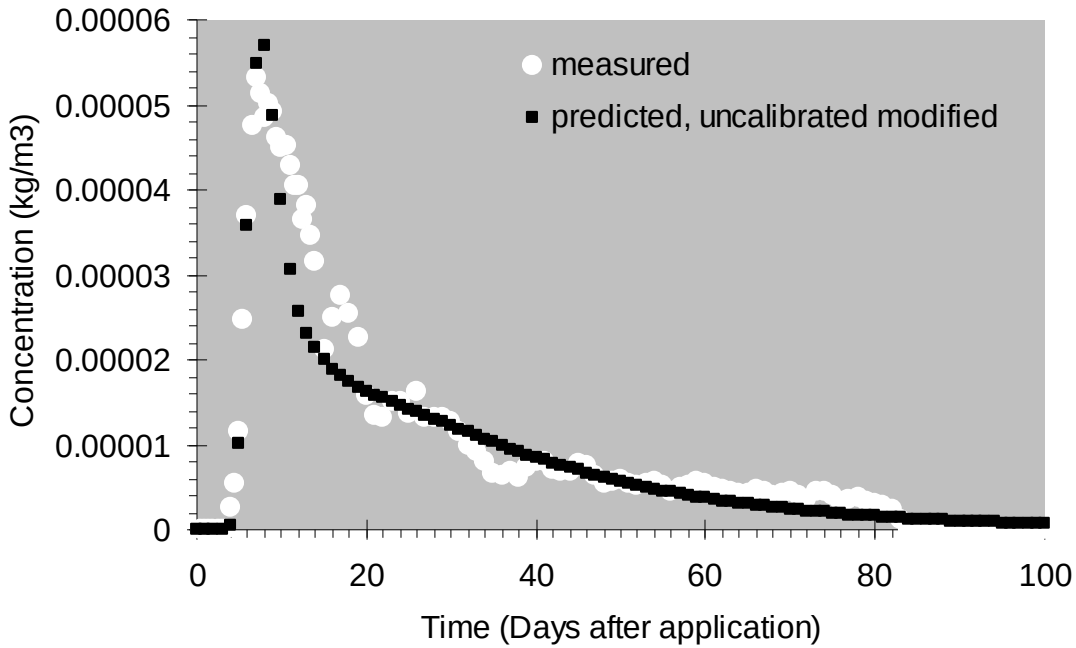
Step 3: Predict breakthrough curves with kinetic sorption parameters derived from static lab incubation study (transport parameter fixed at Step 1)



Undisturbed Soil Columns

Step 3: Predict breakthrough curves with kinetic sorption parameters derived from static lab incubation study (transport parameter fixed at Step 1)

Compound B breakthrough for Birkenheide soil (loamy sand), shift of 0.5 eq sorption to neq (total sorption conserved)



RLP Agroscience & Bayer Cropscience Experiments

First results of column experiments indicate that

- **TDS parameter derived from static experiment are in agreement with transport experiment**

Futher evaluation of data set is ongoing

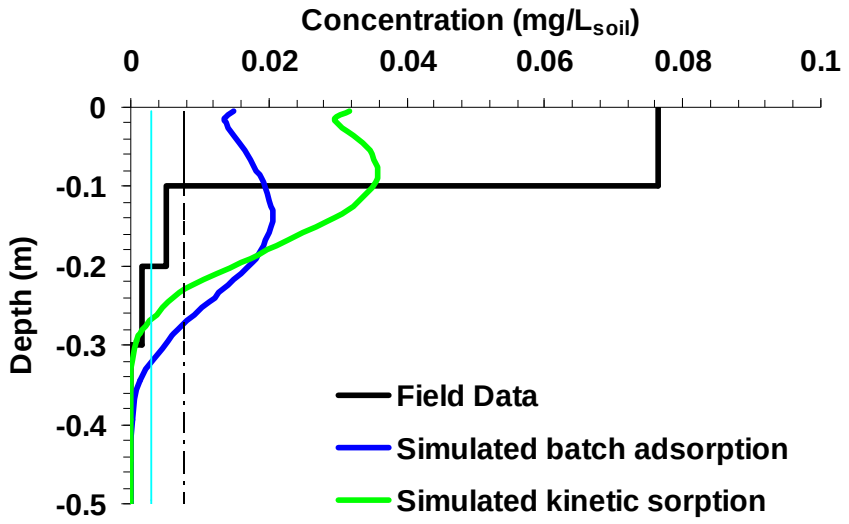
Combination of Laboratory and Field Data

- **Often bulk $DT50_{field}$ and $DT50_{lab}$ are different**
- **$DT50_{field}$ considered as higher tier**
- **No indications of different TDS parameter in lab and field (except $DT50_{eq}$)**
- **Most advantageous way to include TDS is combination of lab TDS parameter with field degradation**
- **However uncertainty remains because there can not be a strict proof of individual equivalence**
- **This can be overcome by additional validation step**

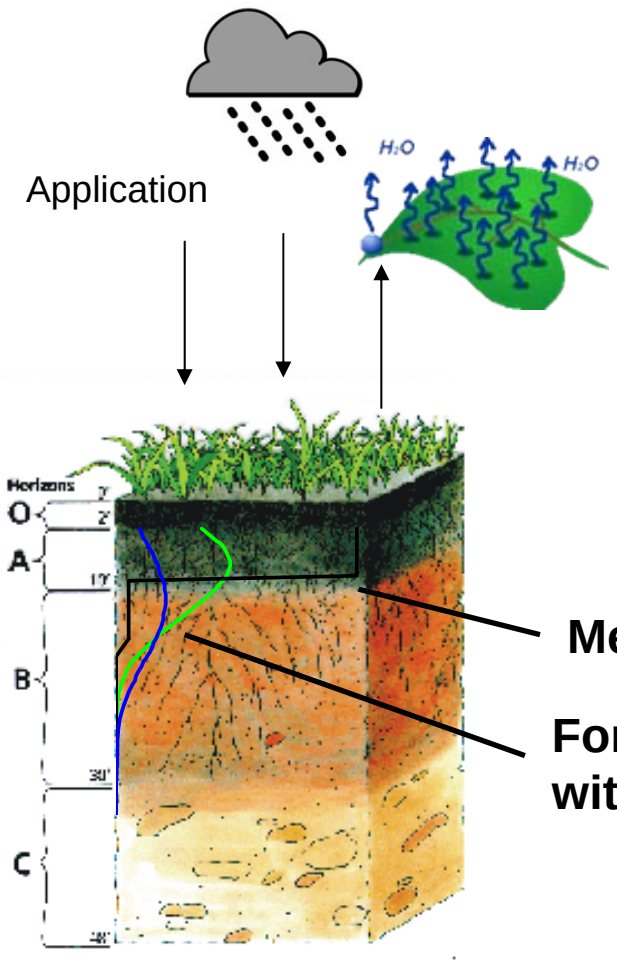
Validation of degradation and sorption parameters

Validation of degradation and sorption parameters

- **comparison with measured depth profiles in field dissipation studies**
- **individual validation site by site for a number time points**



Validation of degradation and sorption parameters



Measured

Forward simulation with model (PEARL)

Uncertainty assessment

Site specific parameters and driving forces

- **Climate data (precipitation, potential evapotranspiration)**
- **Application**
- **Crop data**
- **Soil data (OC, hydraulic properties, bulk density, dispersivity)**

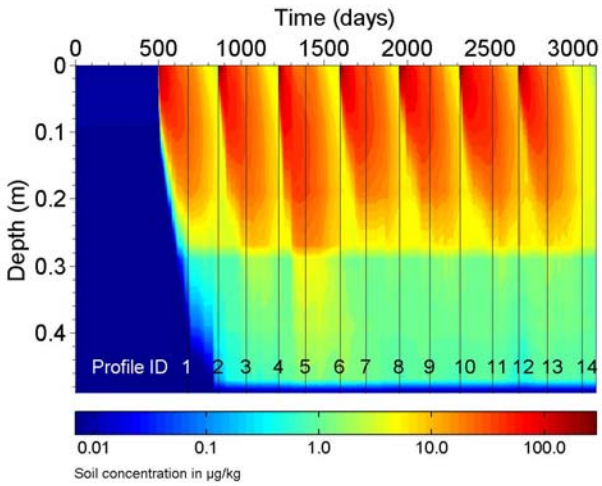
Degradation and sorption parameter to be validated

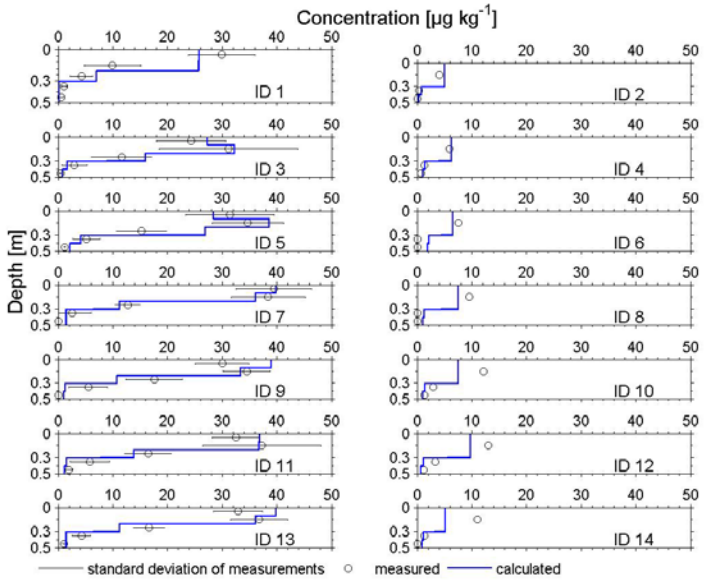
Uncertainty of Estimated Scenario Parameters

Example: Estimated hydraulic properties (Kahl and Hammel, 2010)

For three field accumulation studies running over 7 years

- **hydraulic parameters were estimated from original ROSETTA and HYPRES for the respective texture classes**
- **DT50 and Kom were estimated inversely**
- **PEARL 3.3.3 and PEST**





Uncertainty of Estimated Scenario Parameters

Example: Estimated hydraulic properties (Kahl and Hammel, 2010)

Single hydraulic parameters were varied within realistic boundaries (10th and 90th percentile in UNSODA soil data base), grouped by main textures (Sand, Silt)

Averaged maximal change in hydr. parameters, DT_{50}, and k_{om} values in all three soils

	α	n	θ_r	k_s	θ_s
	1433%	60%	345%	2593%	24%
DT_{50}	21%	17%	18%	3%	2%
K_{om}	2%	2%	3%	2%	1%

- **Influence on DT_{50} due to water content via Walker equation**
- **No effect on Kom**

Uncertainty of Estimated Scenario Parameters

Example: Estimated hydraulic properties (Kahl and Hammel, 2010)

Conclusions

- **Moderate effect of hydraulic parameters on degradation (DT50)**
- **Marginal effect of hydraulic parameters on chemical transport (Kom)**

Uncertainty of Estimated Scenario Parameters

Other site specific parameters and driving forces (work ongoing)

- **Rainfall: We expect marginal effect on DT50, direct effect on Kom**
- **Potential evapotranspiration: Same as for rainfall**
- **Soil bulk density, dispersivity**
- **Plant parameters**

Conclusions

- **Comparison of TDS measurements under static lab, kinetic lab and field conditions indicate no systematic deviation**
- **Statistical reliable TDS parameter from field measurements could not be derived due to insufficient data quality for this purpose**
- **The combination of lab (kinetic sorption) and field (degradation) appears most advantageous in terms of accuracy and effort**
- **Remaining uncertainties accompanied with this combination can be assessed by individual validation**



Thank you very much for your kind attention.

Backup