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# KINETIC SORPTION OF PESTICIDES IN SOIL: BRIDGING FROM LABORATORY TO THE FIELD

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## Agenda/ Content

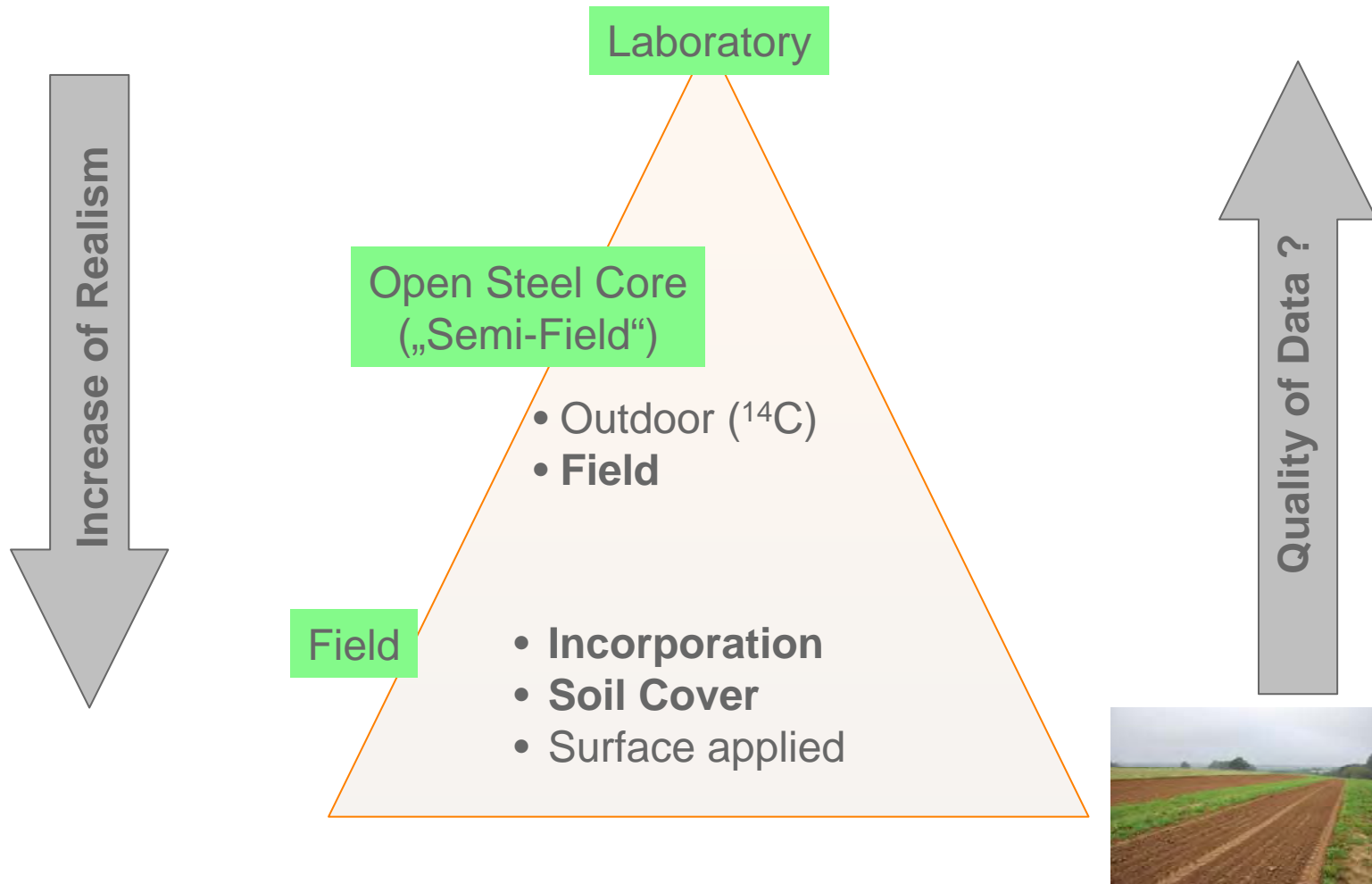
- Key Questions
- Concept: Experiments Bridging from Laboratory to Field Conditions
- Experimental Methods
- Results: Data Quality, Kinetic Sorption Behaviour and Parameters
- Conclusions



# Key Questions

1. Does kinetic sorption exist under field conditions?
2. Is it possible to quantify kinetic sorption in field experiments?
3. Is the standard model appropriate to describe the increase of sorption?
4. Does the experimental method used for incorporation (soil cover or tillage) influence the result?
5. Is the effect of kinetic sorption in field comparable to laboratory?

# General Experimental Concept





# Key Features of Experiments

	Method	Soil condition	Moisture	Temperature	Test substance	Application	Initial distribution	Sampling	Effort
<b>Lab aged sorption study</b>	OECD 307 Beulke et al. (2010)	<b>Sieved</b>	40-60% WHCmax <b>constant</b>	20 °C <b>constant</b>	<sup>14</sup> C label	<b>Defined dosing</b>	<b>Mix</b>	<b>Entire flask</b>	<b>low</b>
<b>Steel core Outdoor <sup>14</sup>C</b>		Undisturbed	Variable (time and depth)	Variable (time and depth)	<sup>14</sup> C label	Defined dosing	Soil surface, covered with 3 cm soil	Entire soil core, aliquots	<b>medium</b>
<b>Steel core Field</b>		Undisturbed (4)	Variable (time and depth)	Variable (time and depth)	Non-labeled	Defined dosing	Soil surface, covered with 3 cm soil	Entire soil core, aliquots	<b>medium</b>
<b>Field Incorporation</b>	EFSA Guidance 2011	<b>Tilled Rotary harrow (1) Sowing comb (2)</b>	<b>Variable (time and depth)</b>	<b>Variable (time and depth)</b>	Non-labeled	<b>Formulated, Spray</b>	<b>Mix 0-10 cm</b>	<b>Sampling 0-15 cm</b>	<b>high</b>
<b>Field Soil cover</b>	EFSA Guidance 2011	<b>Undisturbed (3)</b>	<b>Variable (time and depth)</b>	<b>Variable (time and depth)</b>	Non-labeled	<b>Formulated, Spray</b>	<b>Soil surface, covered with 3 cm soil</b>	<b>Sampling 0-15 cm</b>	<b>high</b>



# Field Experiments

- Site: Silt loam soil, 1 % OC, located in North Rhine-Westphalia (Germany)
- Time of application: Autumn 2010
- Duration: 60 days
- Sampling: 10 soil cores combined to mixed sample at day 0, 3, 7, 14, 31, 60  
0-15 cm and 15-30 cm depth
- Chemical analyses: Homogenization, 2 aliquots, shaken for 24 h with aqueous  $\text{CaCl}_2$  solution (OECD 106), extraction with organic solvents
- Weather data: Station on-site
- Climatic conditions: 169 mm rainfall during experimental period, 11.8 °C average temperature

# Field: Spray Application



# Field Experiments: Incorporation with Rotary Harrow





# Field Experiments: Incorporation with Sowing Comb



# Field Experiments: Covering with Soil



# Semi-Field Experiments: Confined Cores Covered with Soil





# Derivation of Kinetic Sorption Parameters

Kinetic sorption model: As implemented in FOCUS PEARL

Kinetic sorption parameter\*

- Fraction of non-equilibrium sorption  $f_{NE}$
- Rate constant  $k_{des}$  for transfer between equilibrium and non-equilibrium phase
- Equilibrium  $K_{om}$  ( $K_{om,eq}$ )
- $DT50_{eq}$  (DT50 in liquid and equilibrium sorption phase)

Method of evaluation: Inverse modelling (PEST-PEARL) accounting for transport and sorption processes under transient soil moisture and temperature conditions

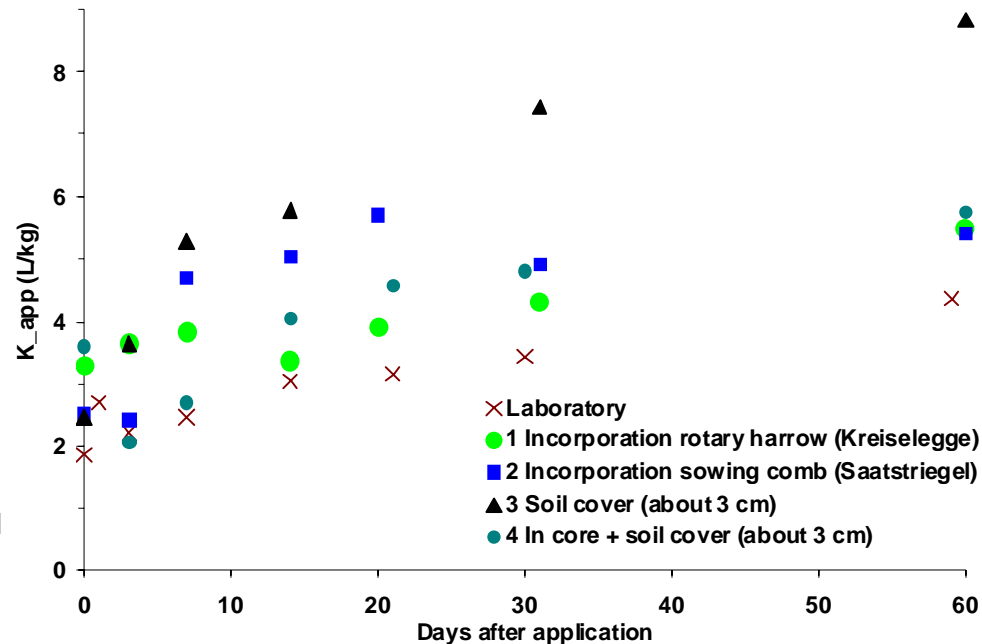
Early data points (day 0 and 3) were excluded

More details: See poster "INVERSE ESTIMATION OF KINETIC SORPTION PARAMETERS FROM A FIELD STUDY" by Hammel et al.

\* Freundlich exponent is actually also kinetic sorption parameter but typically taken from batch sorption study on same soil. Conceptually  $K_{om,eq}$  and Freundlich exponent are identical with the standard batch values

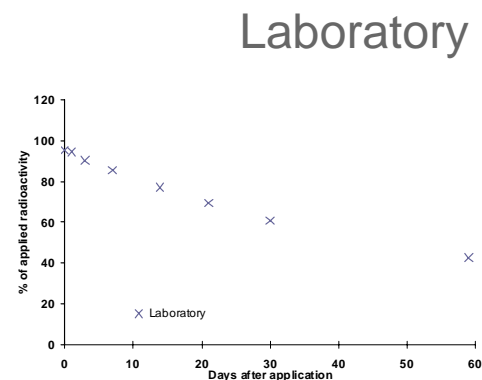
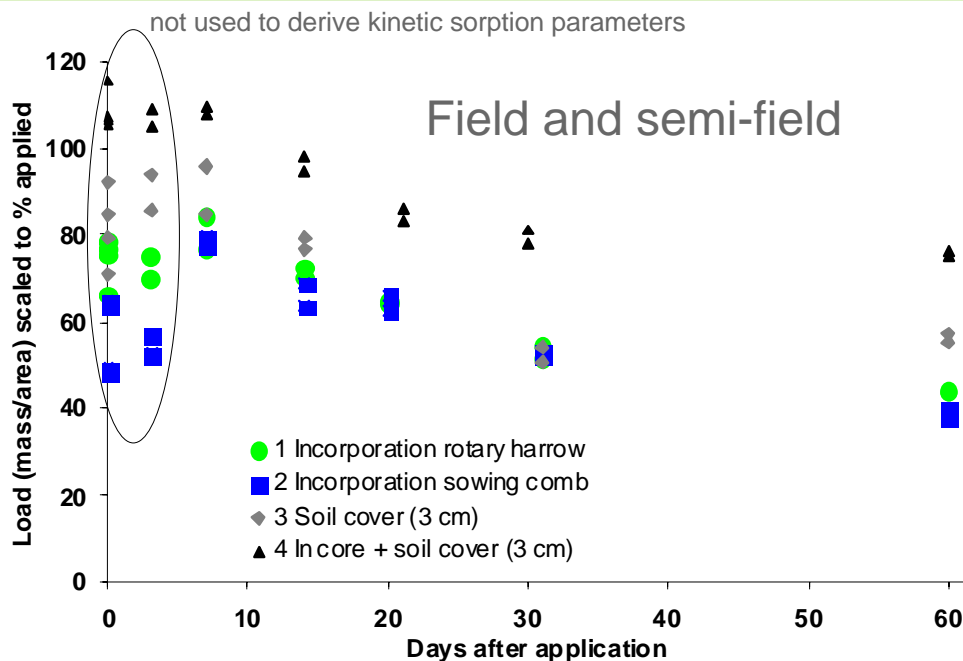
# Results: Distribution Coefficient as Function of Time

$$K_{app} = C_{sorbed} / C_{liquid}$$



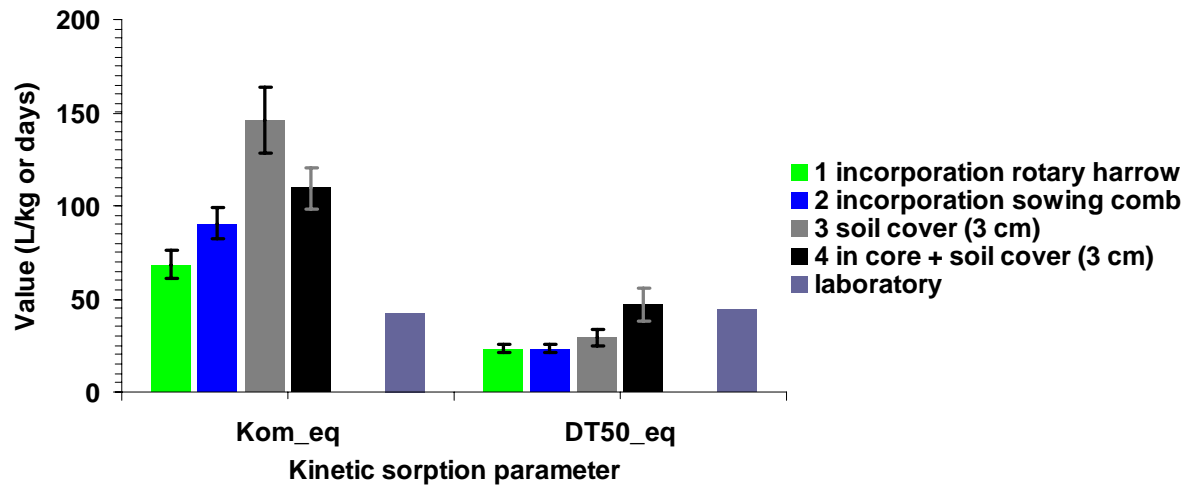
- Sorption distribution coefficient ( $K_{app}$ ) increases substantially with time for all experimental variants
- $K_{app}$  obtained from field and semi-field experiments tend to higher values than those obtained from laboratory experiment
- Data from field and semi-field experiments exhibit more scatter than laboratory data

# Results: Total Residues as Function of Time

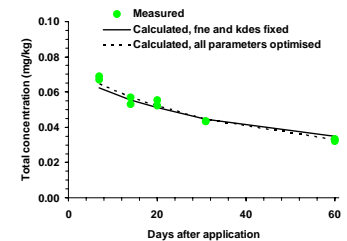


- Similar intensity of decline for all field and semi-field experiments, somewhat different residue levels
- Large scatter at early time points
- Moderate scatter at later time points (>3 days), yet larger as in laboratory study

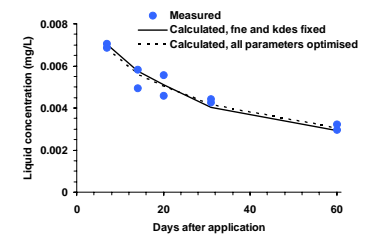
# Results: Kinetic Sorption Parameters (1)



Total mass

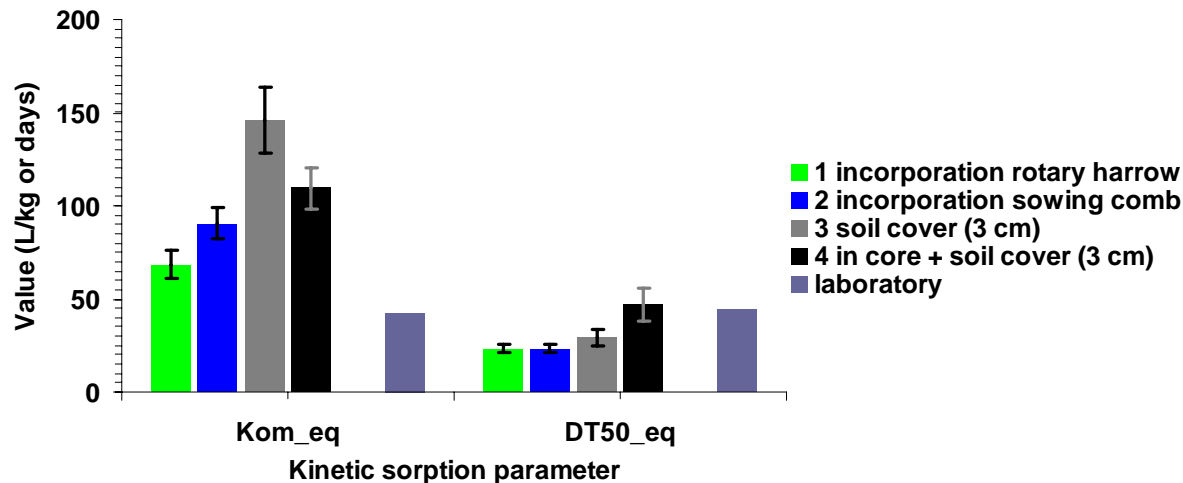


Liquid concentration

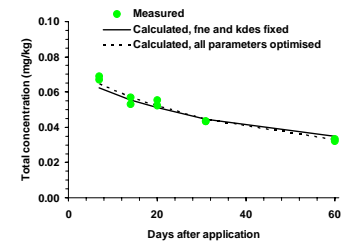


- Not all kinetic sorption parameters can be identified simultaneously (only 5 time points)
- But fixing intrinsic kinetic sorption parameters ( $f_{NE}$  and  $k_{des}$ ) to values obtained in laboratory results in good fits and reliable estimates for equilibrium  $K_{om}$  ( $K_{om,eq}$ ) and DT50 in liquid and equilibrium sorption phase ( $DT50_{eq}$ )
- Laboratory and field derived kinetic sorption parameters may be combined

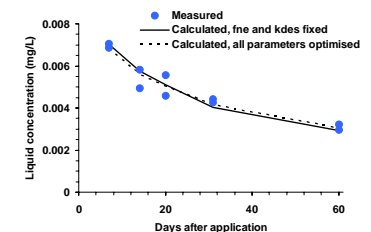
# Results: Kinetic Sorption Parameters (2)



Total mass



Liquid concentration



- $DT50_{eq}$  of field variants is **lower** compared to laboratory and semi-field variants
- $K_{om,eq}$  of field and semi-field variants is **higher** compared to laboratory variant
- In present case, use of exclusively laboratory-derived kinetic sorption parameter set results in much more conservative groundwater exposure assessment than including more realistic field-derived parameters





# Conclusions (1)

1. Does kinetic sorption exist under field conditions?
  - ▶ Under field conditions a clear increase of sorption with time was observed which is consistent with the behaviour under laboratory conditions.
2. Is it possible to quantify kinetic sorption in field experiments?
  - ▶ With a limited data set it was already possible to reliably determine 2 key parameters ( $DT50_{eq}$ ,  $K_{om, eq}$ ).
  - Although the scatter will be somewhat larger than under laboratory conditions we are confident to be able to determine all (4) kinetic sorption parameters for a longer experimental period/more samples from a carefully designed field study.
  - If equivalence of specific parameters derived from laboratory and field experiments can be confirmed, combination of laboratory and field derived parameter may be an efficient and robust approach. Large scatter at early time points is unsatisfying and requires further examination.



## Conclusions (2)

3. Is the standard model appropriate to describe the increase of sorption?
  - ▶ The established kinetic sorption model used was well consistent with the observed data.
4. Does the experimental method used for incorporation (soil cover or tillage) influence the result?
  - ▶ The results in terms of residues, increase of sorption with time and kinetic sorption parameters were similar for all incorporation variants. Occasional numerical deviations are not attributed to systematic effects caused by the method for incorporation.



## Conclusions (3)

### 5. Is the effect of kinetic sorption in field comparable to laboratory?

► The qualitative manifestation of kinetic sorption in laboratory and field is very similar.

In the case studied, the field data lead to kinetic sorption parameters which indicate faster degradation and higher (equilibrium) sorption.

► As **simpler** yet **conservative** approach laboratory derived values for  $f_{NE}$ ,  $k_{des}$  and  $K_{om, eq}$  may be combined with a field derived degradation half-life  $DT50_{eq}$

- optimisation of  $DT50_{eq}$  based on total concentration or mass observed in the field with  $f_{NE}$ ,  $k_{des}$  and  $K_{om, eq}$  fixed to laboratory derived values
- **simple** because only total concentrations are required
- **conservative** because  $K_{om, eq}$  from laboratory data was lower than from field data

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