

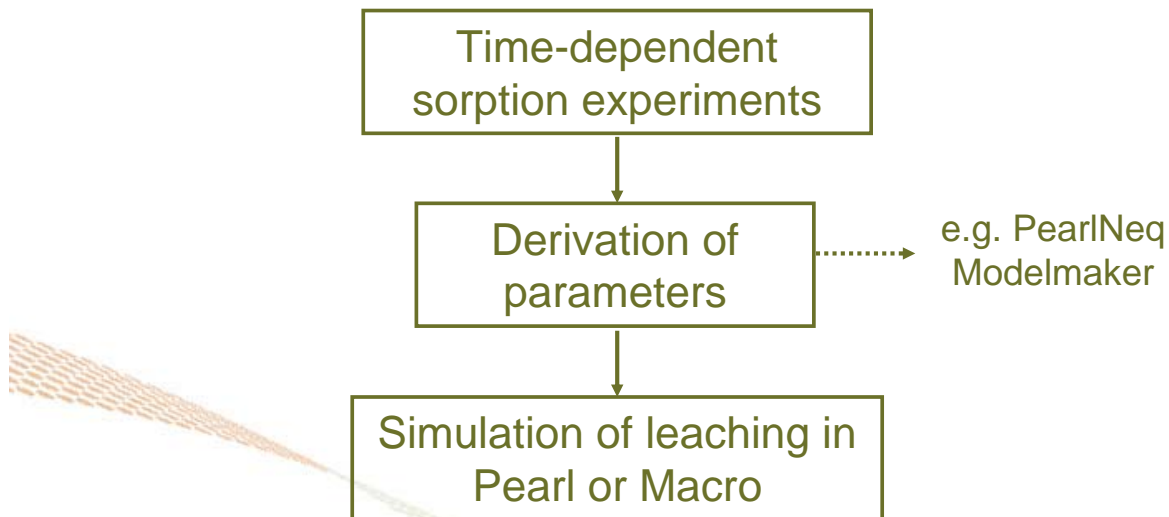
Methods for time-dependent sorption measurements

*Wendy van Beinum, Sabine Beulke
Gareth Bryning, Simon Cardwell (Fera)
Jos Boesten, Mechteld ter Horst (Alterra)*

Risk assessment modelling

- Time-dependent sorption currently not included in risk assessment at lower tier
- Current practice: Sorption K_{OC} measured in standard batch sorption studies (24-hour shaking)
- Modelling of leaching to groundwater and surface water (Pearl, PRZM, Macro)
- Reality: Increase of sorption with time, less pesticide available for leaching with time
- Need for standardised methods to incorporate in risk assessment

Implementation of time-dependent sorption



Experimental methods

1. Incubation of sieved soil
2. Incubation of soil aggregates
3. Sorption-desorption study in shaken batch

Table 1. Pesticide properties

	K_{oc} (ml g ⁻¹)	DT50 (days)
chlorotoluron	259	43
azoxystrobin	609	85

Table 2. Soil properties

	clay (%)	OC (%)
Wick	14	1.1
Lawford	22	2.3
Salop	48	3.3

1. Incubation of sieved soil

- Pesticide applied onto sieved soil (<2mm) in individual jars (50 g soil per jar)
- Incubated for 1, 3, 7, 14 .. 84 days at 20 ° C at 60% of max water holding capacity
- 3 replicates per incubation period



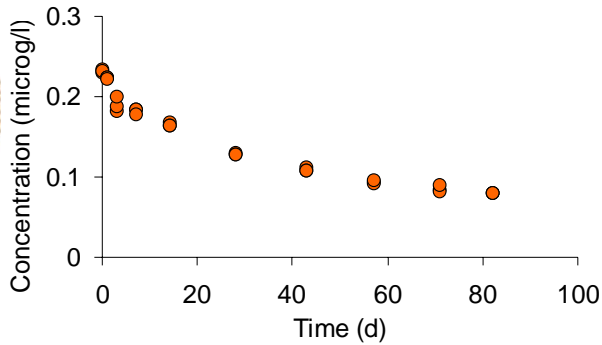
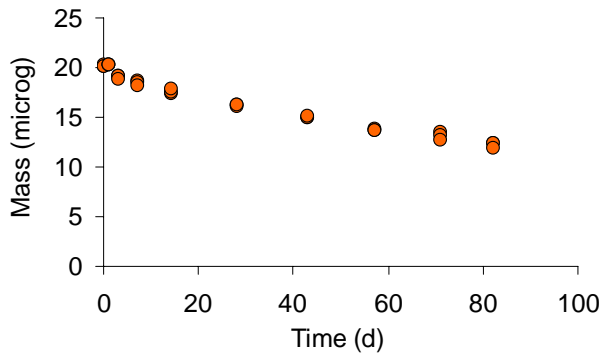
Extraction methods



- Solvent extraction for total pesticide mass
- Methods for extraction available pesticide
 1. Centrifugation method
 2. 1-hour aqueous extraction
 3. 24-hour aqueous extraction
- Analysis by HPLC

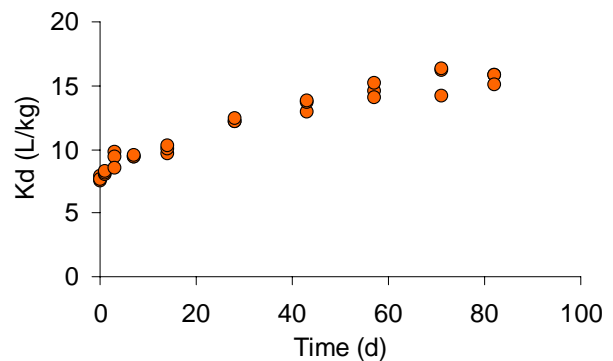
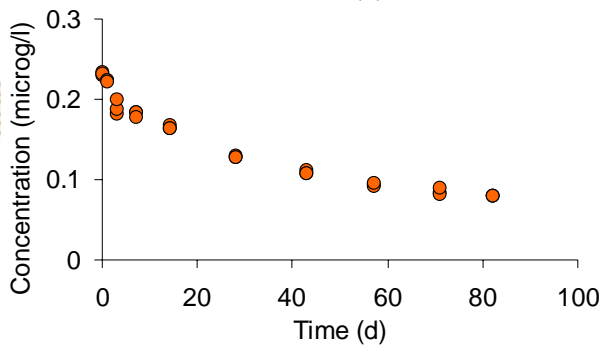
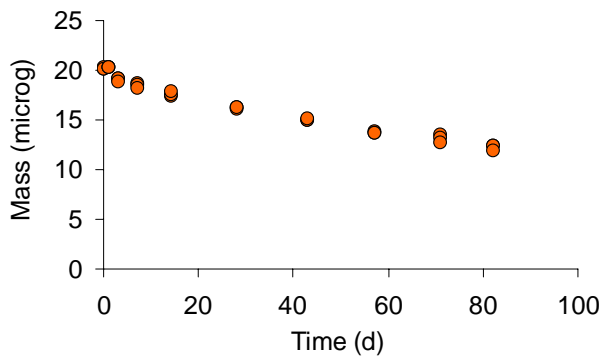
Results

azoxystrobin applied to
sieved Wick soil
24-h aqueous extraction

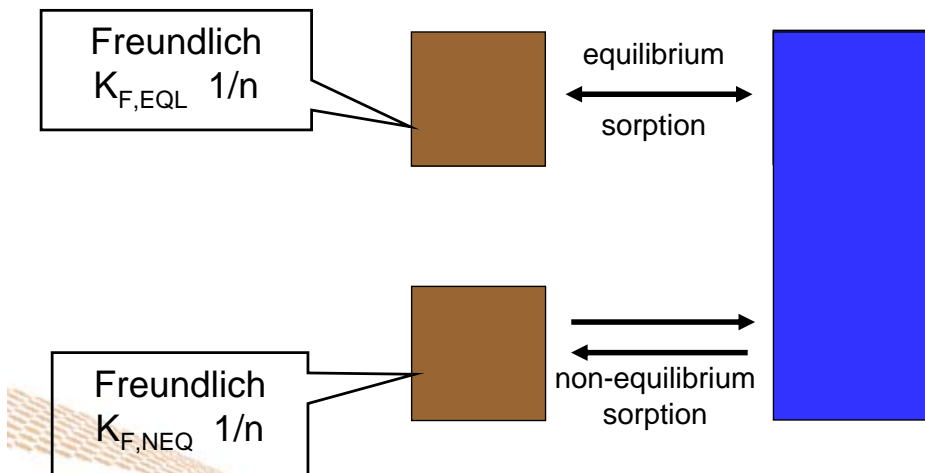


Results

azoxystrobin applied to
sieved Wick soil
24-h aqueous extraction

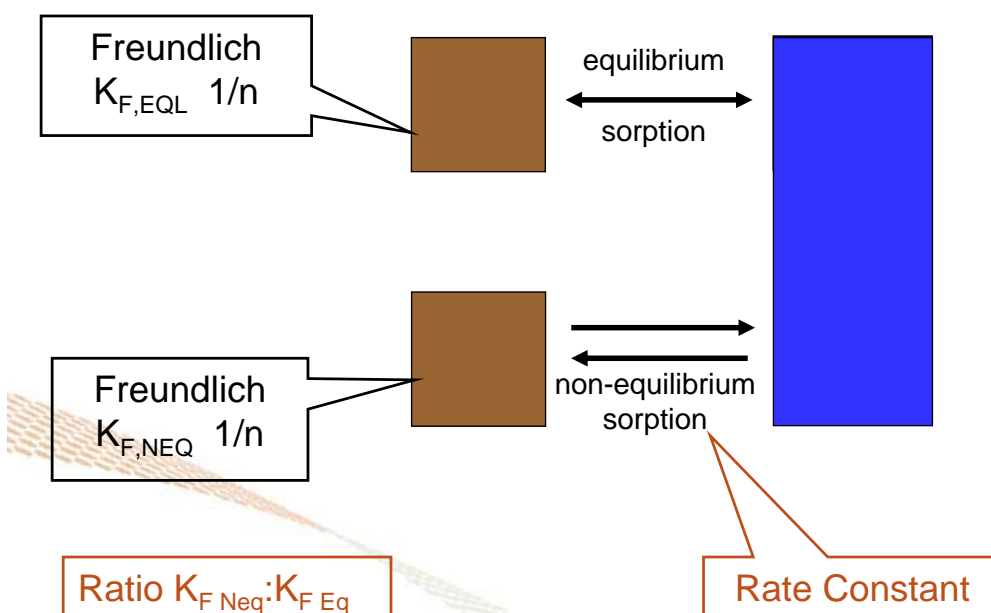


Two-site model (PearlNeq)

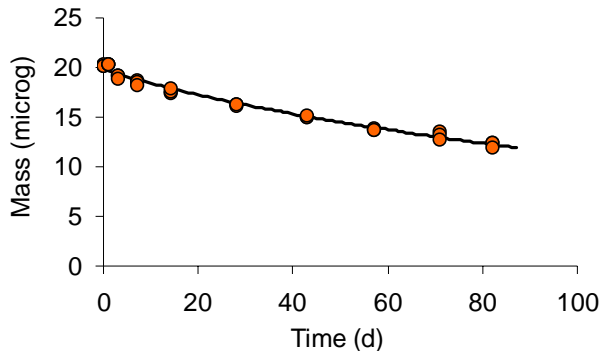


- Definition of equilibrium sorption based on sorption measured in batch sorption experiment

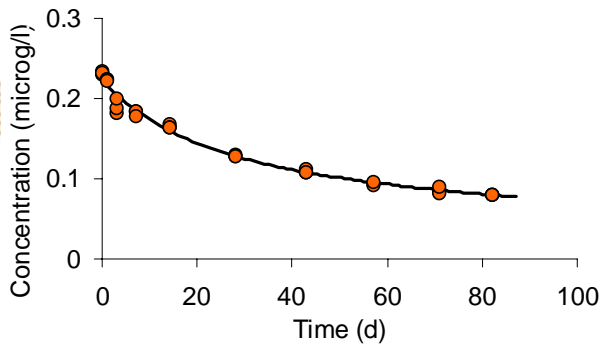
Two-site model (PearlNeq)



Model fitting of parameters

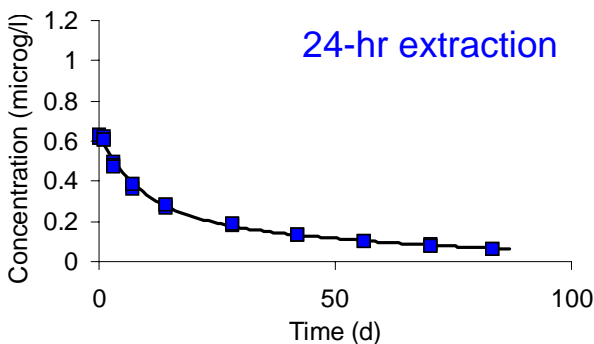
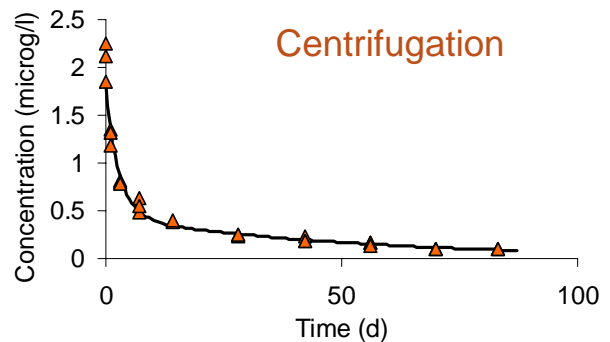
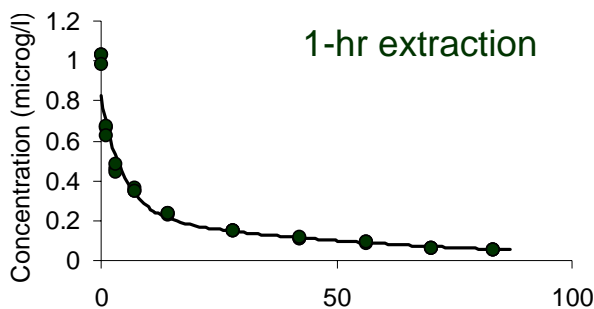


Initial mass = 19.8 μg
 DT50 = 87 d
 Ratio NEQ/EQ = 0.45
 Rate = 0.037 d^{-1}
 $K_{F,EQ} = 2.76 \text{ L kg}^{-1}$



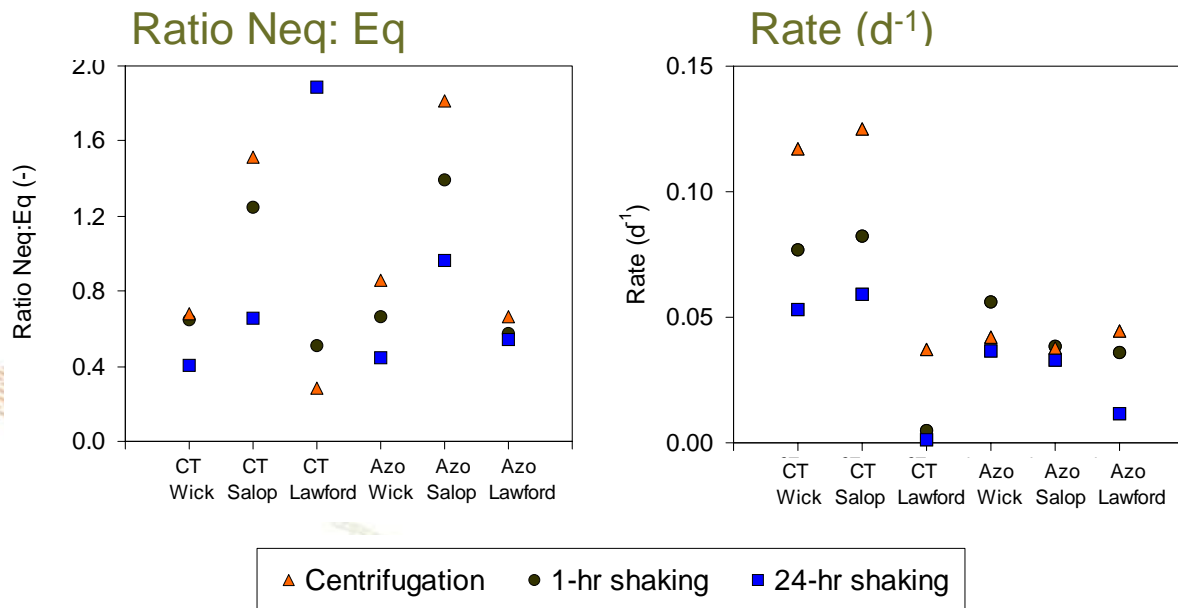
azoxystrobin applied to
sieved Wick soil
24-h aqueous extraction

Comparison extraction methods



- Centrifugation method: Steeper decline in concentration results in larger Rate and Ratio
- Aqueous extraction methods: Adsorption during shaking

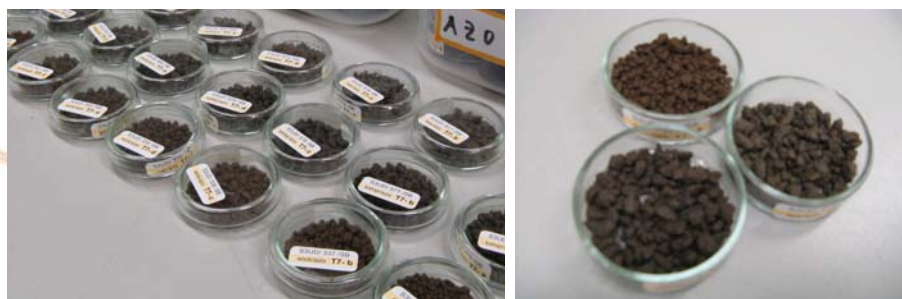
Comparison extraction methods



2. Incubation of aggregates

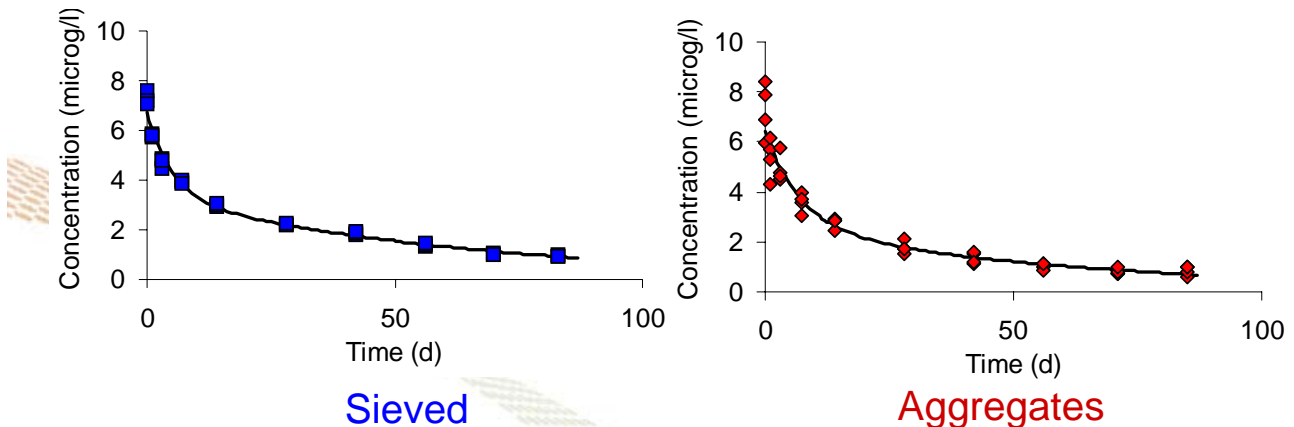
- Method

- Aggregates separated by sieving (3-5 mm)
- Incubation of 10 gram aggregate samples
- Extraction of total mass with solvent and extraction of soil solution by centrifugation



Aggregates vs. sieved soil

- No consistent effect on sorption parameters
- Larger variability between replicates for aggregates
- Aggregate method was more time-consuming

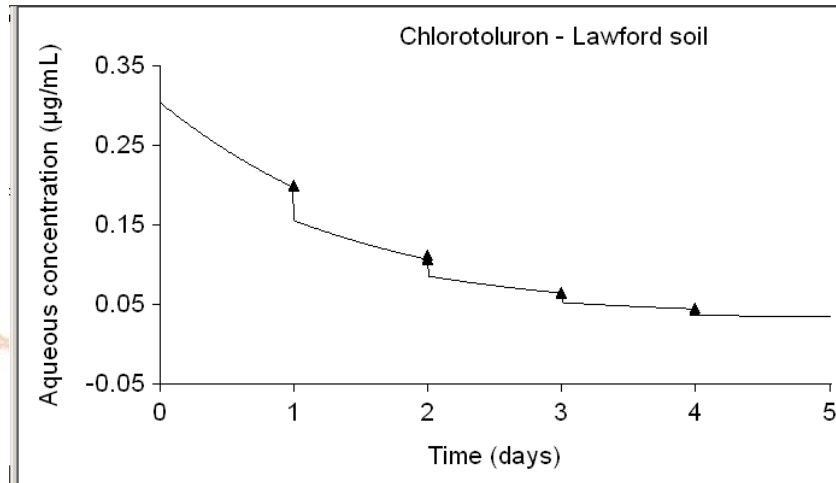


3. Batch sorption-desorption study

- Adsorption step: Pesticide solution was added to soil and shaken gently for 24 hours
- 3 desorption steps: part of solution was replaced by pesticide-free solution, then shaken again for 24 hours
- Pesticide concentration analysed after each step

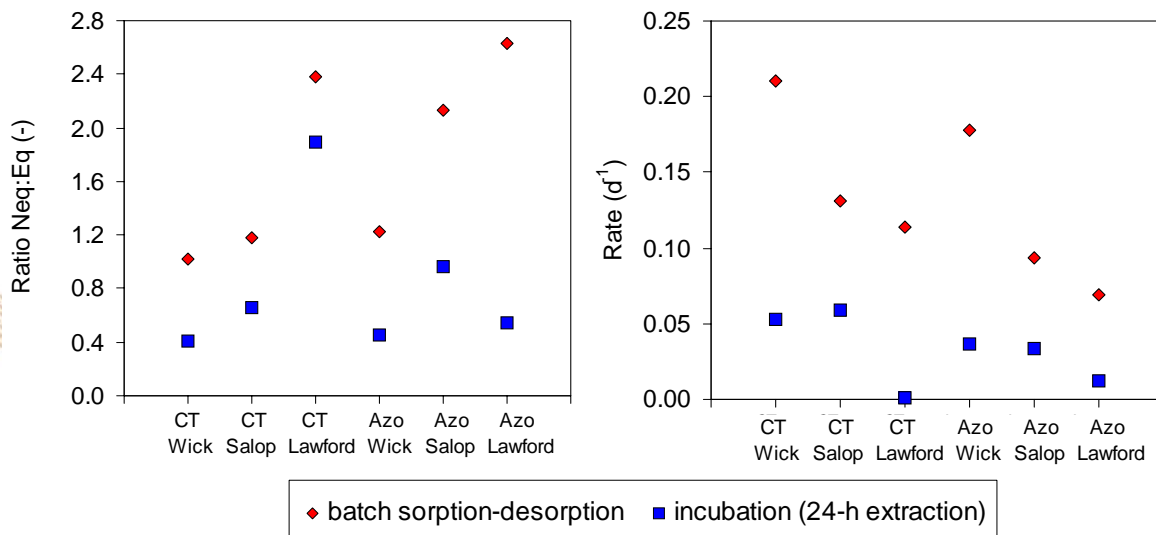
Batch sorption-desorption study

Model fitting in ModelMaker: Rate constant (d^{-1})
and Ratio $Neq:Eq$



Batch sorption-desorption study

More non-equilibrium sorption as in incubated soil



Conclusions

- Time-dependent sorption parameters depend on experimental method
- Need for consistent and reproducible method to determine sorption parameters
- Batch sorption-desorption method overestimates the amount and rate of nonequilibrium sorption
- Incubation of aggregates gives more variable measurements and is more time-consuming

Conclusions

Advantages of incubation study with sieved soil followed by extraction:

- Incubation of moist soil reflects sorption at realistic soil moisture content
- Method could possibly be combined with degradation study
- Method is expected to be reliable and reproducible

Next

- Address model fitting procedures: criteria for data quality, goodness of fit and confidence interval of derived sorption parameters
- Examine if rate and ratio determined by model fitting are reliable for different types of datasets (fast or slow degradation, significant increase in sorption)
- Draft guidance on how time-dependent sorption studies should be conducted, analysed and used in regulatory assessments
- Present draft guidance at stakeholder workshop in February