Degradation behaviour of metazachlor in soil as influenced by different incubation systems

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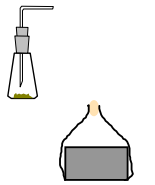
Outline

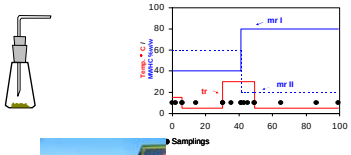
- Incubation systems
- Results
- Conclusions

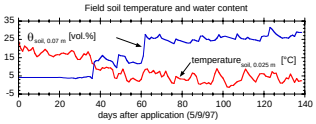
Overview on incubation systems

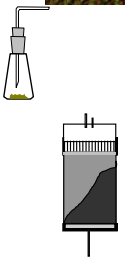
Soil / No.	Incubation system
I / 1	Sieved soil (batch, application on top, constant)
I / 2	Undisturbed 5 cm topsoil (core, application on top, constant)
I / 3	Sieved soil (batch, appl. on top, variable incubation 2 moisture regimes: mr I & mr II, 1 temperature regime: tr)
I / 4	Field (variable) 1) Autumn application (1997): first weeks warm and dry, then cool and wetter 2) Spring application (1998): first weeks temperate and moist, then warmer and dryer
II / 1	Sieved soil (batch, appl. on top + shaking, constant) ^{14}C labelled Metazachlor, 10 °C, 50 % MWHC (=moisture content of equilibrated microlysimeter)
II / 2	Undisturbed Microlysimeter 30cm (constant temp., appl. on top, variable. water flux) ^{14}C labelled Metazachlor, 10°C, bromide tracer, water flow 4 and 8 mm/day , 5 days a week

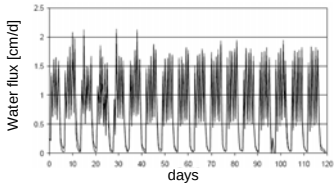


MWHC (%)	temperature (°C) 5	10	15	20	30
20			X		
40		X			X
60				X	
80	X				









DegT$_{50}$ of metazachlor (batch vs core)

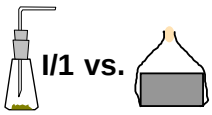
I/1 vs.  I/2

MWHC (%)	temperature (°C) 5	10	15	20	30
20			X		
40		X			X
60				X	
80	X				

Incubation conditions	DegT$_{50}$ at incubation conditions [d]		DegT$_{50}$ normalised to 20°C and pF2 [d]		Ratio core : batch (DegT$_{50}$normalised)
°C / % MWHC	batch (I/1)*	core (I/2)**	**batch (I/1)**	**core (I/2)**	
5 / 80	60	86	**14**	**21**	**1.5**
10 / 40	45	67	**16**	**18**	**1.1**
15 / 20	46	83	**16**	**22**	**1.4**
20 / 60	14	20	**14**	**19**	**1.4**
30 / 40	7	-	**17**	-	**Average 1.3**

* MWHC batch = 31 % w/w
** MWHC core = 21 % w/w

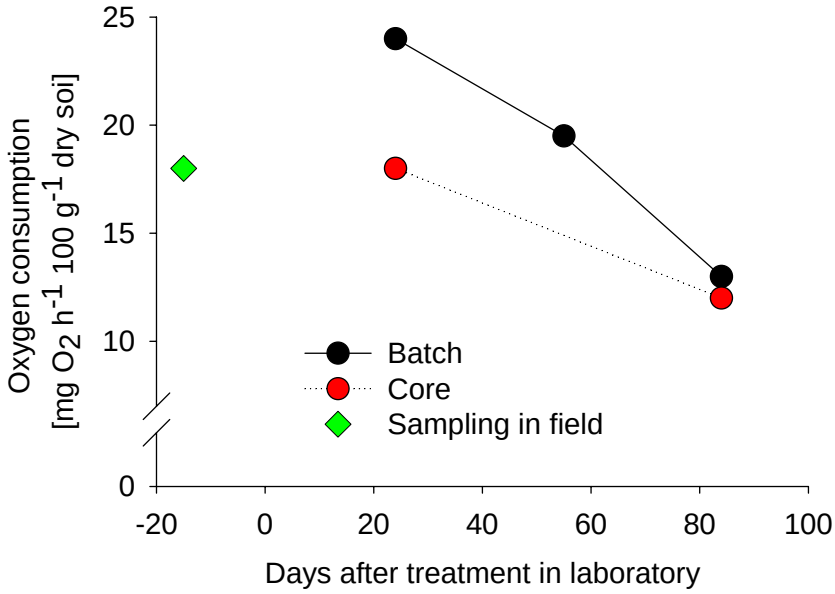
Possible reason for faster degradation in batch compared to core



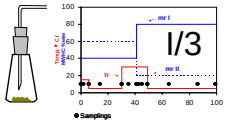
I/1 vs. I/2

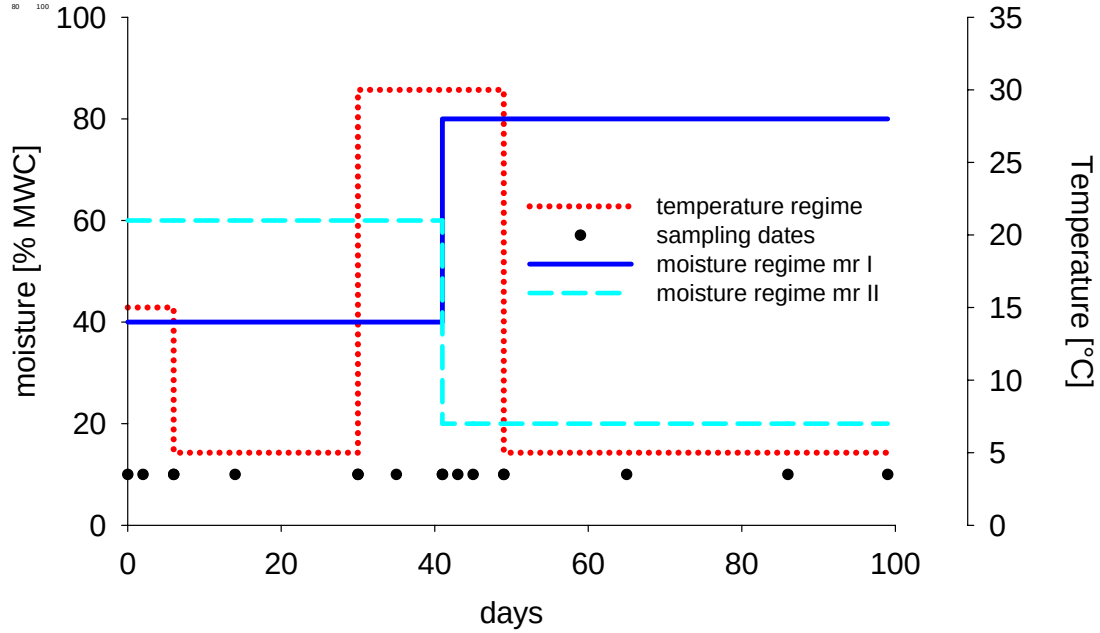
Increase of microbial activity
by stirring the soil
preparing the batch
for incubation

Intact soil core
conserved the microbial
status from the field

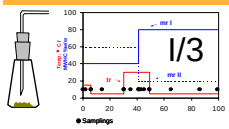


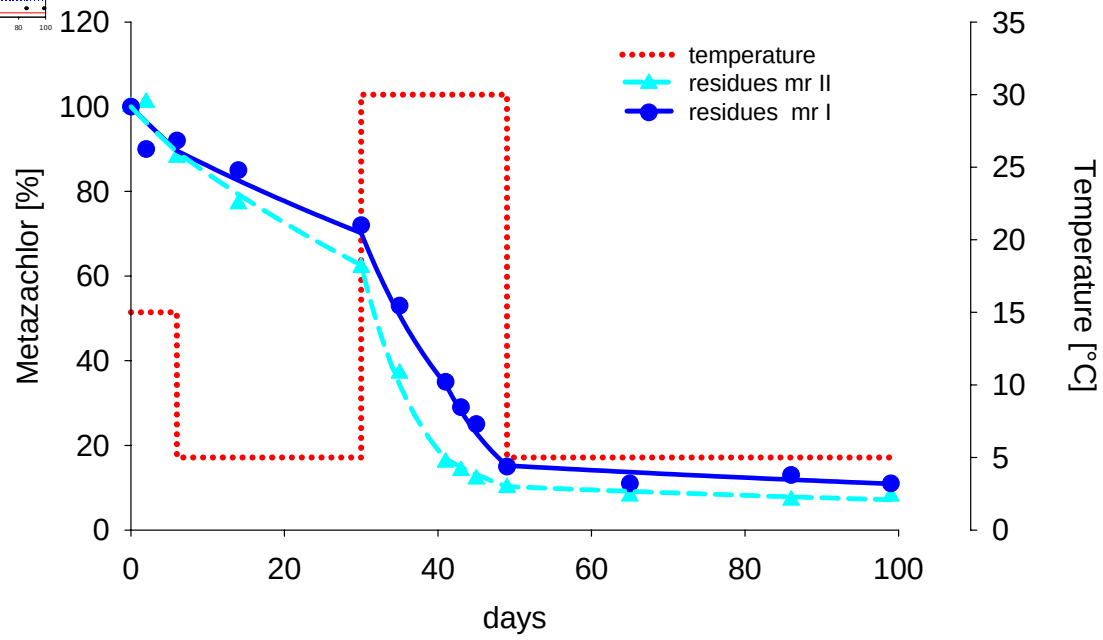
Variable temperature and moisture regime



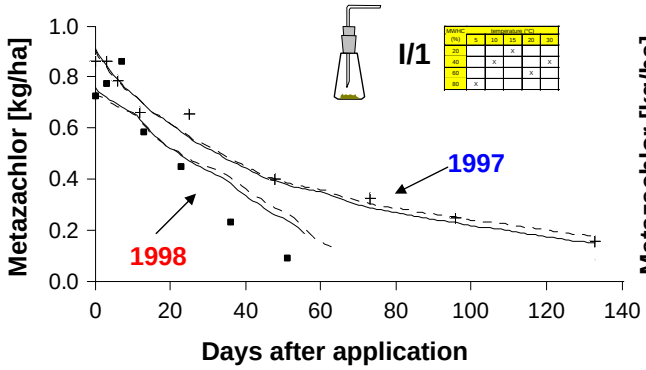


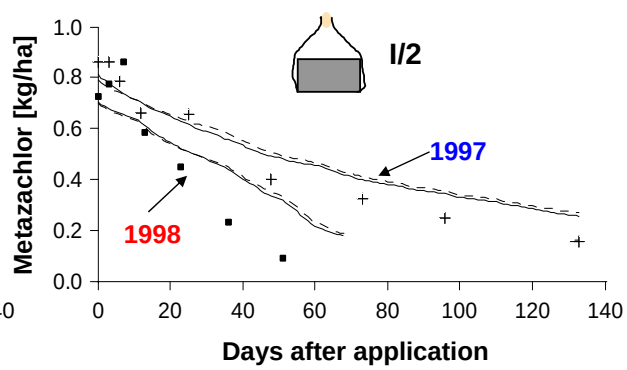
Measured and fitted degradation of Metazachlor with variable temperature and moisture regime

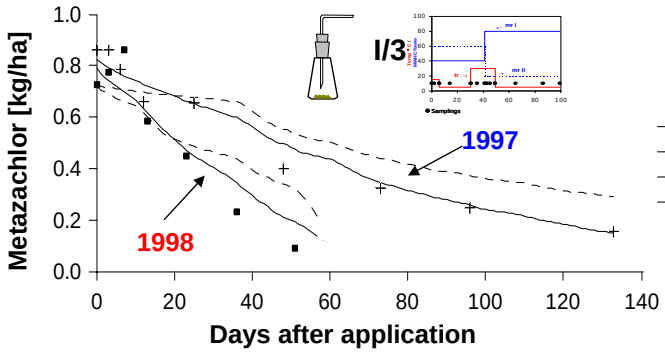


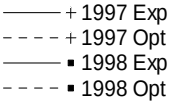


Degradation of Metazachlor in the field and it‘s simulation based on different lab incubation systems









Short summary

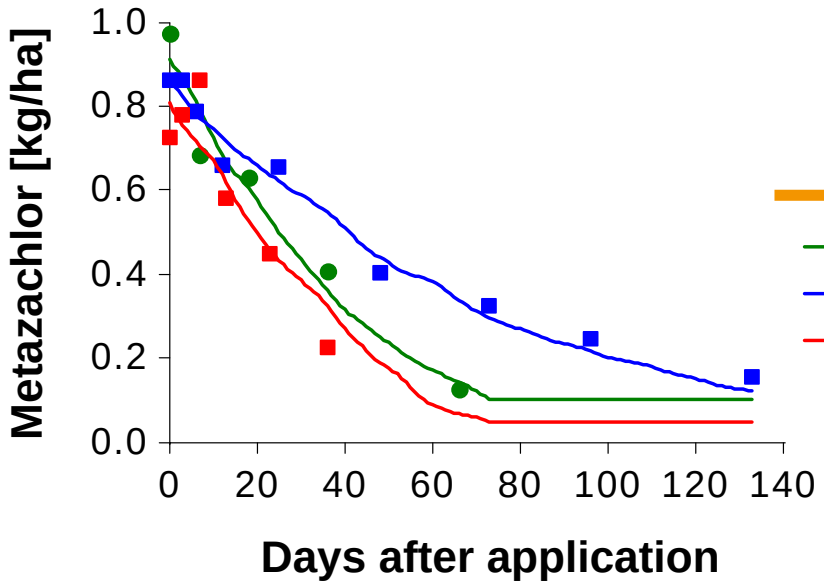
- Batch incubation system at different moisture and temperature levels provided reasonable parameters for prediction of persistence of Metazachlor in the field
- Batch incubation with time variable temperature and moisture regimes provided a slightly better parameters for prediction of persistence.
  In terms of reducing effort it could be a superior experimental design compared to the full scale combination of incubation conditions.
  Setting of sampling times need thorough planing.
- Incubation of undisturbed soil cores provided parameters, which turned out to be worse for prediction of persistence in the field.

Parameter estimation from field studies: individual and simultaneous fit by inverse modelling

- 3 field dissipation trials:
  - „Meckenheim“ (soil I): autumn 1997
  - „Meckenheim“ (soil I): spring 1998
  - „Nienwohlde“ (near Braunschweig): spring 1994 *
- Site Meckenheim: continuous measurement of soil moisture / temperature
- Site Nienwohlde: simulation of soil moisture / temperature using weather data

* Beulke S. (1998): Untersuchung und mathematische Beschreibung des Abbaus von Herbiziden im Boden in Abhängigkeit von Wirkstoffverfügbarkeit, mikrobieller Biomasse und Aktivität. Phd Thesis, University Braunschweig .

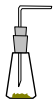
Individual and simultaneous fit of Metazachlor degradation from field studies



Trial / fit	$DegT_{50}$* [d]
Simultaneous	**14.7**
1994 spring	**12.8**
1997 autumn	**17.9**
1998 spring	**9.8**

*@20°C, pF2, Q10=2.2

Comparative study with batch and microlysimeter incubation (soil II)

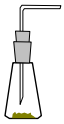
Degradation study:  II/1

- Sieved soil (batch, constant)
  10 °C, 50 % MWHC (=moisture of equilibrated microlysimeter)
- application of a first order degradation reaction
  to the data of totally extracted metazachlor

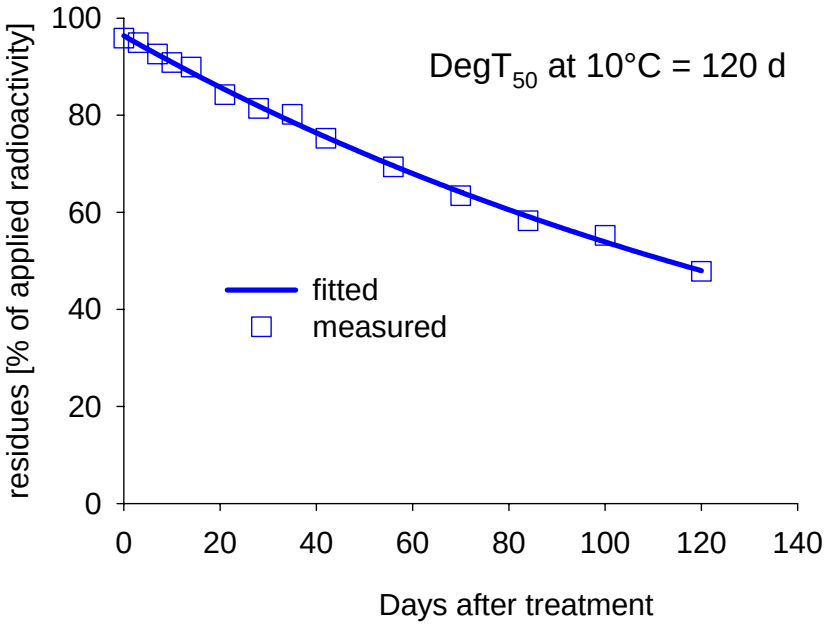
Microlysimeter:  II/2

- Undisturbed Microlysimeter 30cm; 10°C, bromide tracer, discontinuous irrigation 4 and 8 mm/day on 5 days a week
- applying the convection-dispersion-equation to the BTCs of bromide
- applying the convection-dispersion-equation for kinetic adsorption (two-site-model) to the BTCs of metazachlor

Degradation of Metazachlor in soil II (batch incubation at 10 °C)

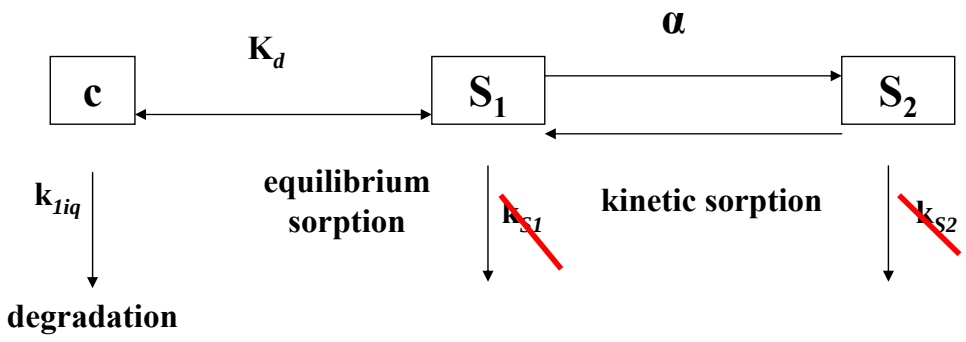


II/1



Microlysimeter: assumptions for parameter estimation for sorption and degradation of Metazachlor

II/2



- Degradation only in liquid phase (so no degradation of sorbed substance)
- Stationary flux conditions
- Linear sorption
- DT50 (total) estimated from simulated residual mass

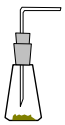
$$\frac{\partial M_{MTZ}}{\partial t} = \frac{\partial \sum c + S_1 + S_2}{\partial t}$$

Fit of the convection-dispersion-equation to the BTCs of bromide and the two-site-model to the BTCs of metazachlor

II/2

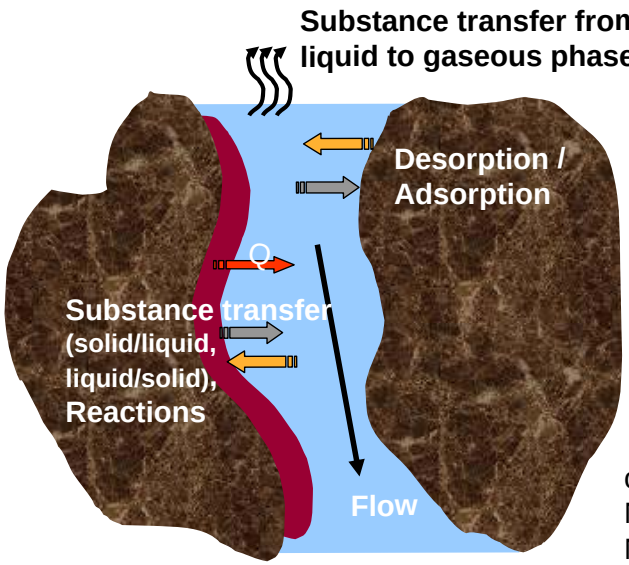
irrigation	4 mm/d (I)	4 mm/d (II)	8 mm/d (I)	8 mm/d (II)
$K_{d\ app}$ [ml/g]	1.9	1.3	4.8	3.7
DT_{50} liq at 10°C [d]	6.3	5.7	3.1	2.1
DT_{50} total at 10°C [d]	37	24	41	11

DT50 of Metazachlor in batch and microlysimeter incubation systems

		DT50 at 10°C	$DT50_{normalised}$ * at 20°C
 II/1	Batch	120 d	47 d
 II/2	Microlysimeter	11 - 41 d	4 -16 d

* Q10 of 2.58

Processes on meso- and micro-scales in soil considering biofilm theory



- Exchange processes take place much more effectively on a advective basis than on a diffusive one.
- Advective transport stimulates microbial activity.
  -> availability of nutrients
  -> microorganisms get rid of possible toxic by- & endproducts

Conclusions

- Standard studies to determine degradation are a good starting point
- Incubation regime with varying temperature and moisture may help to reduce experimental efforts (sampling points !)
- Higher tigher experimental setups like microlysimeters and equivalent mathematical evaluations deliver more realistic parameters
- A thorough kinetic evaluation of field dissipation studies is the most promisimg procedure to obtain realistic degradation values
  - Joint evaluation of multiple studies (population statistics) seems to be promising
  - Biofilm theory ?
    -> worthwile to explore in pesticide fate arena (esp. water sediment)

Thank you for your attention