On the Use of Field Dissipation Trials to Derive Degradation Kinetics for Use in Exposure Modelling

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Introduction

Terrestrial field dissipation (tfd) trials are a proven way to assess the dissipation behaviour of plant protection products under realistic field conditions similar to actual use conditions. They are therefore increasingly used to derive degradation kinetics for use in simulation models to predict environmental exposure, especially leaching to groundwater.

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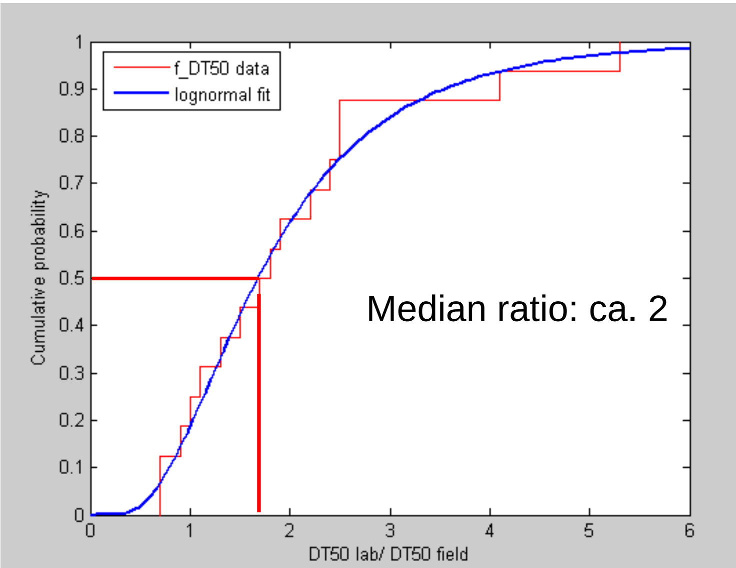
However

Since tfd studies are performed under variable conditions and include several degradation and dissipation routes, the extraction of degradation kinetics for use in a mechanistical simulation model poses several problems.

DT50 from laboratory and field studies

Ratio between DT50 lab and DT50 field

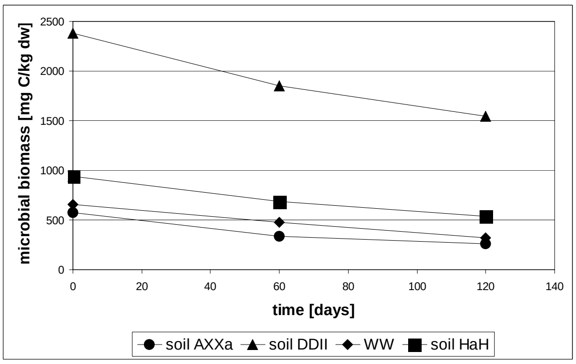


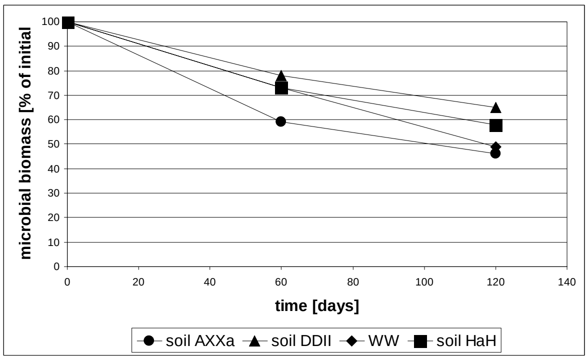
(geo)Mean DT50

16 Pesticides

Comparable evaluations for field and laboratory

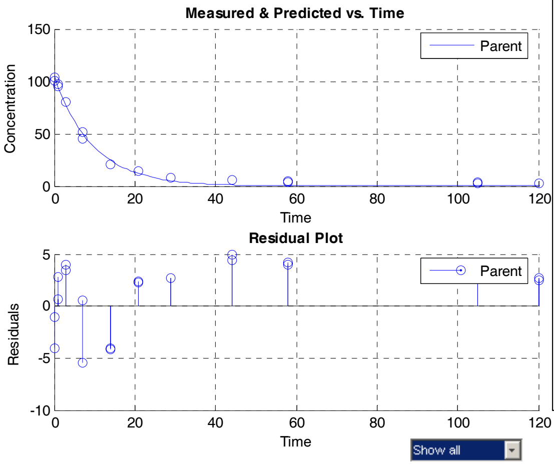
Decline of biomass in a laboratory study

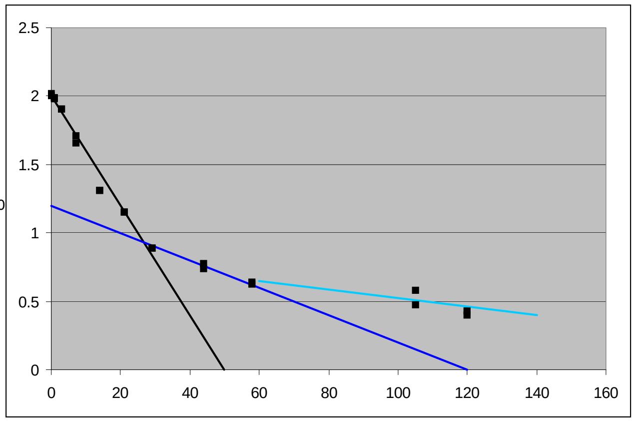




➔Relative decline is very consistent for different soils

Decline in degradation rate in a laboratory study





Logarithmic plot Log c = f(t)

Effect clearly seen plot

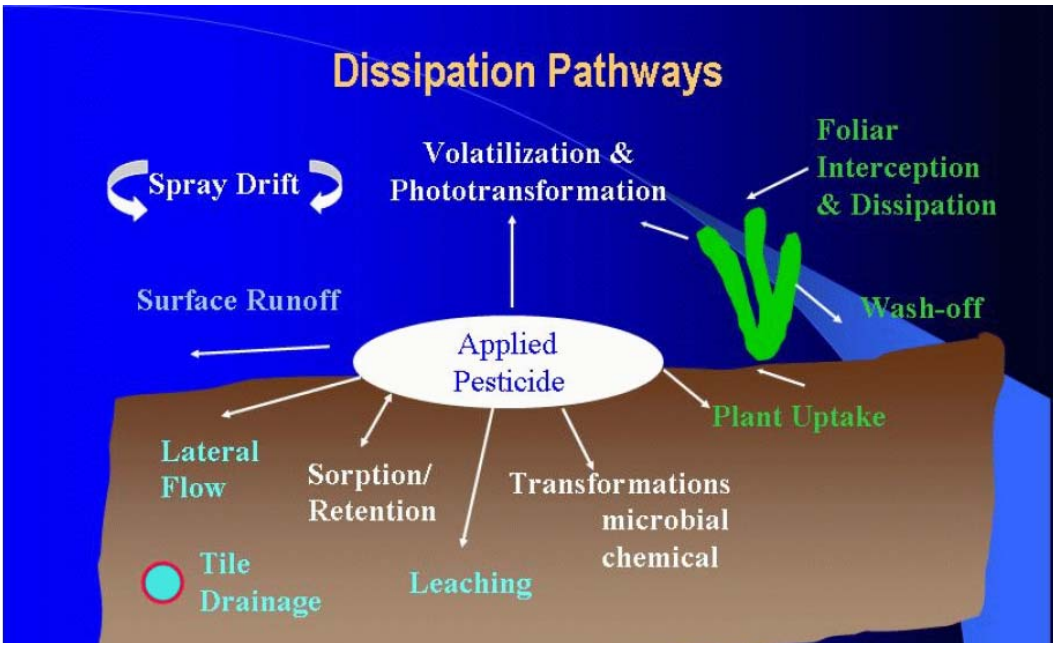
Cannot be quantitatively linked to

decline in biomass

Other causes for the mostly better degradation have been discussed

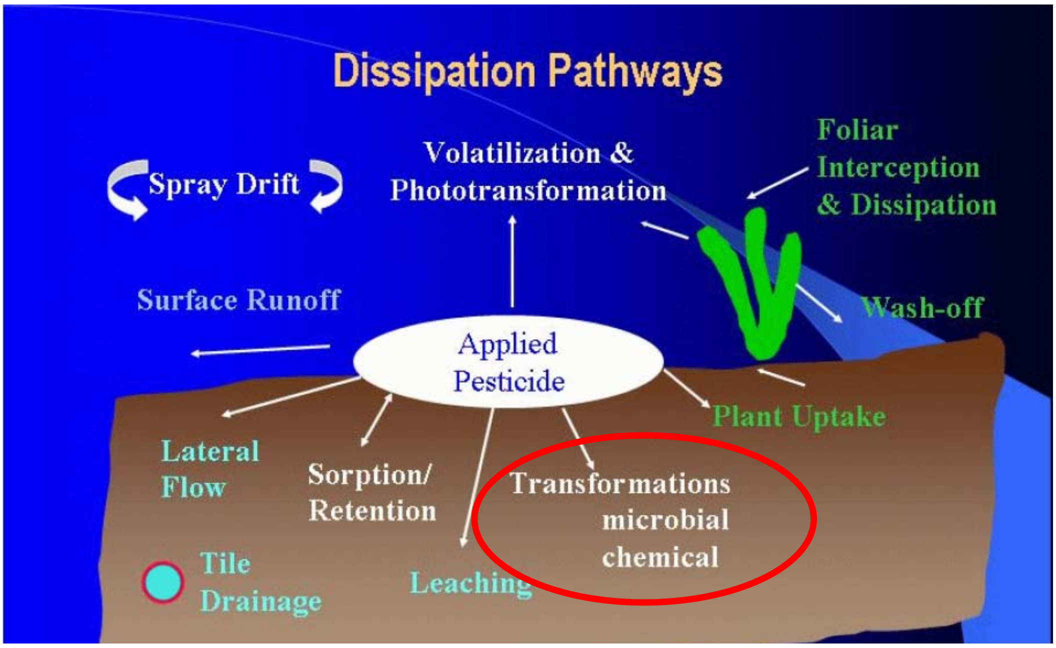
(Kubiak et al. 1995, Gottesbüren et al. 2009)

Conceptual Model of the dissipation of a chemical in the field



From:
NAFTA Guidance Document for Conducting Terrestrial Field Dissipation Studies
US-EPA and PMRA, 2006

Conceptual Model of the dissipation of a chemical in the field



From:
NAFTA Guidance Document for Conducting Terrestrial Field Dissipation Studies
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Objectives

- NAFTA guidance: Broad overview of all dissipation and degradation processes determining the fate of a chemical in the field.
- Determination of model input parameters: Isolation of kinetic parameters that can be used in fate models.

Options

- Evaluation procedures to extract “pure” biodegradation constants
  - Leaching
  - Plant uptake
  - Sorption/retention
  - Photolysis/Volatilisation
- Exclusion of dissipation pathways by suitable experimental design
  - Surface run-off
  - Lateral flow
  - Plant interception
  - Photolysis/Volatilisation
- “Lumping” processes into a DisT50 and appropriate consideration in the fate model
  - Plant uptake

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Simulation of a tfd study:

Calculate the raw results of a tfd study with a simulation model

➔ Residues in the soil column as function of time

➔ "True" process parameters (= model inputs)

Evaluate simulated results using standard procedures

Compare evaluation of the simulated results with original model inputs

Forward modelling with

- model input parameters from simulation
- "true" process parameters (original model inputs)

Effect of leaching on DT50

Model:	PEARL 3.3.3
Scenario:	FOCUS scenario Kremsmuenster
Application rate:	100g a.i. / ha , application to soil
Application date:	April 15^{th}
Crop:	Gras, emergence 7 days after application
Model compound:	**DT50 = 20 d**
	Kom = 10 L/kg, 1/n = 0.9

Properties chosen to generate significant transport:

PECgw = 0.30 µg/L

Simulated tfd study

Substance amounts in each soil layer are calculated

for each sampling time:

Depth [cm]	Time [days] → 0	3	7	14	28	42	56	70	90	110
10	99.12	82.89	65.74	56.70	44.77	33.59	18.92	12.75	2.73	1.25
20	<LOD	12.55	24.33	24.58	19.48	14.44	15.44	12.46	5.21	2.59
30	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	4.00	3.43	5.44	3.31
40	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1.25	1.25	1.25	1.25

(Amounts given as % of applied)

Simulated tfd study (2)

Assuming Analytics fulfills only the minimum requirements:

LOQ = 5% of applied

LOD = ½ LOQ

Depth [cm]	Time [days] → 0	3	7	14	28	42	56	70	90	110
10	99.12	82.89	65.74	56.70	44.77	33.59	18.92	12.75	<LOQ	<LOD
20	<LOD	12.55	24.33	24.58	19.48	14.44	15.44	12.46	5.21	<LOQ
30		<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOQ	5.44	<LOQ
40							<LOD	<LOD	<LOD	<LOD

(Amounts given as % of applied)

Simulated tfd study (3)

Evaluation without consideration of values below LOQ and LOD:

Normalisation: Time step method
Kinetics program: KinGUI v 1.1

Depth [cm]	0	3	7	14	28	42	56	70	90	110
	Time [days] →									
10	99.12	82.89	65.74	56.70	44.77	33.59	18.92	12.75		
20		12.55	24.33	24.58	19.48	14.44	15.44	12.46	5.21	
30									5.44	
40										

➔ DT50 = 17.7 d (= - 11% vs input value)

(Amounts given as % of applied)

Simulated tfd study (4)

Evaluation following FOCUS for values below LOQ and LOD:

Normalisation: Time step method
Kinetics program: KinGUI v 1.1

Depth [cm]	0	3	7	14	28	42	56	70	90	110
	Time [days] →									
10	99.12	82.89	65.74	56.70	44.77	33.59	18.92	12.75	2.73	1.25
20	1.25	12.55	24.33	24.58	19.48	14.44	15.44	12.46	5.21	2.59
30	0.00	1.25	1.25	1.25	1.25	1.25	4.00	3.43	5.44	3.31
40	0.00	0.00	0.00	0.00	0.00	0.00	1.25	1.25	1.25	1.25

➔DT50 = 19.4 d (= - 3% vs input value)
➔FOCUS kinetics rules work properly

Effect of plant uptake on DT50

Parameters of the simulated tfd study

Model:	PEARL 3.3.3
Scenario:	FOCUS scenario Kremsmuenster
Application rate:	100g a.i. / ha , application to soil
Application date:	April 15th
Crop:	Gras, emergence 7 days after application
Model compound:	**DT50 = 20 d**
	Kom = 10 L/kg, 1/n = 0.9
	TSCF = 0.5

TSCF is the model input in PEARL that determines crop uptake

Simulated tfd study – plant uptake

Evaluation

Normalisation:	Time step method
Kinetics program:	KinGUI v 1.1

➔ **DT50 = 17.9 d (-10% vs input value)**

Effect on Leaching:

PECgw = 0.19 µg/L (- 35% vs result with input value)

Simple correction:

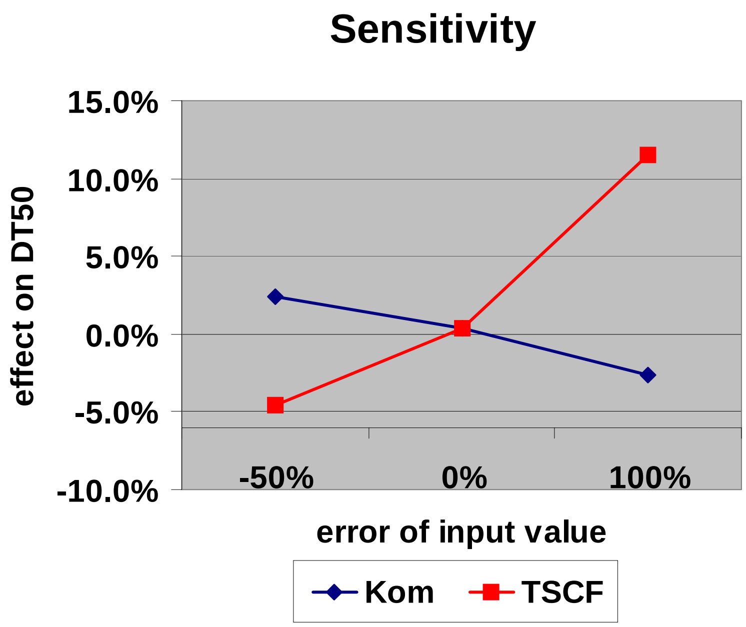
Calculate Leaching without crop uptake (set TSCF = 0)

Grass:	PECgw = 0.28 µg/L (- 6% vs result with input value)
Cereals:	- 12% vs result with input value)
Potatoes:	- 19% vs result with input value)
Vines:	- 29% vs result with input value)

Simulated tfd study – plant uptake (2)

Better correction:
Evaluate tfd study with inverse modelling

➔ **DT50 = 20.1 d (+0.4% vs input value)**



Photolysis and Volatilisation

Surface processes: Very different from chemical or microbial degradation

➔ “Lumping” into a DisT50 not an option

Both processes are not (well) described by current fate models

Options

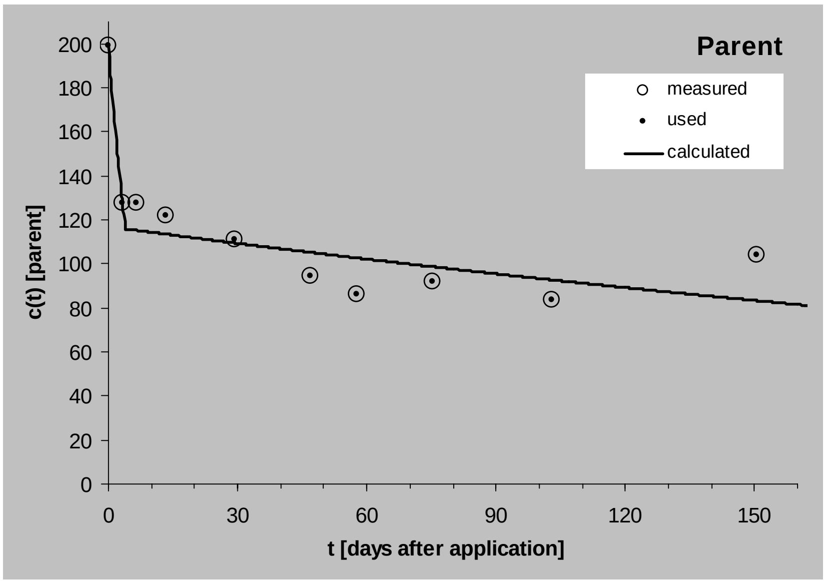
A) Exclusion by experimental design
Incorporate compound into top 5 cm
➔ Always best option, if surface processes are not important for the real application situation

B) Isolate from biphasic degradation curves

Photolysis and Volatilisation (2)

Spray application to the soil surface

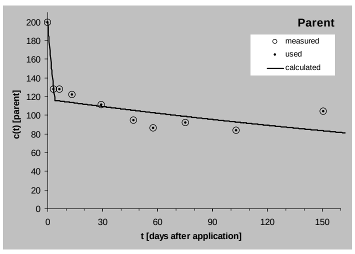
Result of a tfd study



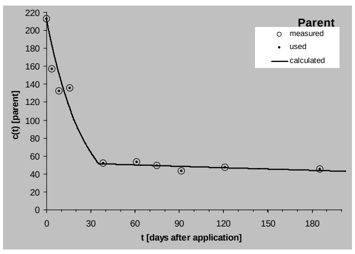
Photolysis and Volatilisation (3)

Spray application to the soil surface

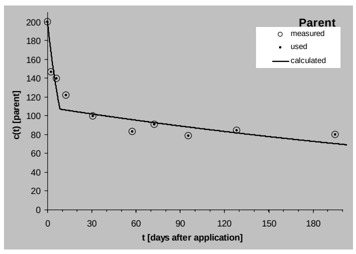
Result of a tfd study



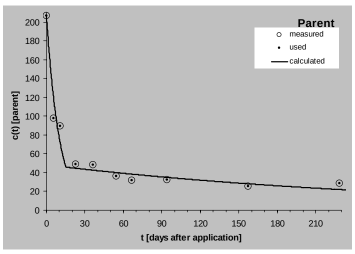
France



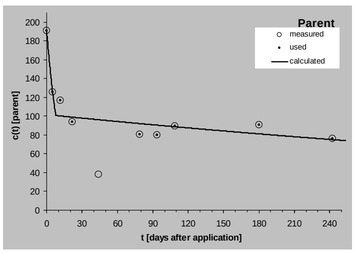
Germany I



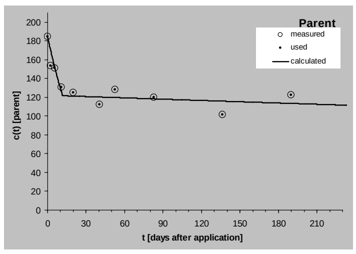
Germany II



Italy



Spain



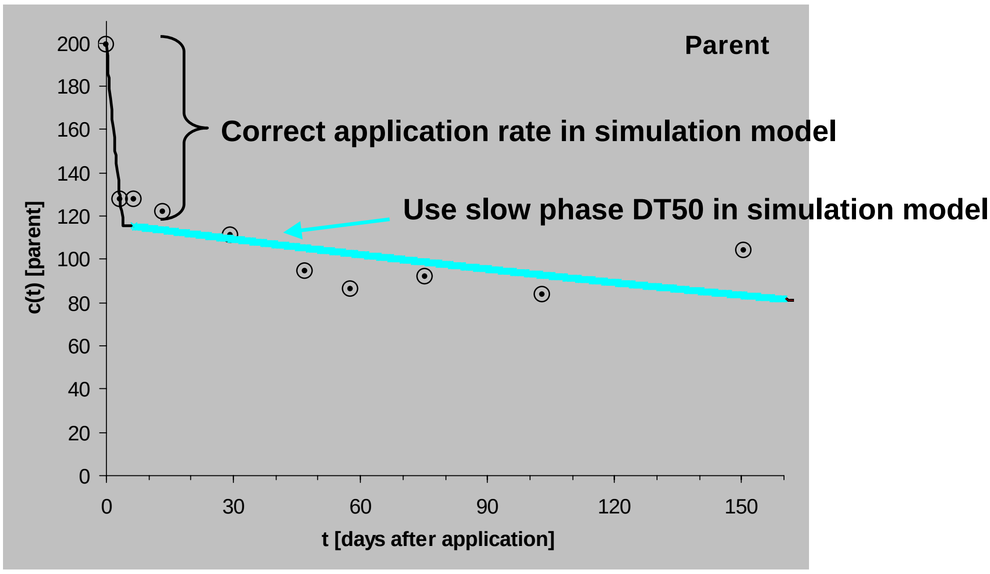
UK

Photolysis and Volatilisation (4)

Consistent fast initial decline between 33 and 78% on all study sites:

➔Initial decline cannot be included in DT50 for modelling

➔If appropriate under application conditions application rate in modelling can be corrected for initil decline.



Conclusion

- Terrestrial field dissipation (tfd) studies frequently show faster degradation of pesticides than laboratory experiments.
- Several reasons for this have been discussed:
  - Decline of microbial activity over time in the laboratory
  - Transport processes and dynamic conditions in the field
- Tfd studies include degradation and dissipation processes other than biodegradation.
- Care must be taken either to exclude these by appropriate experimental design or evaluation procedures.
- If the experimental design is changed to exclude processes, the conditions of the field study must still remain realistic for the real use conditions.
- Use of “lumped” dissipation half lifes (DisT50) is another option which can be used, but care must be taken that this has no undue effect when DisT50 is used in predictive models.

Thank you very much for your kind attention.